WITTECK DEVELOPMENT INC.
2640 South Sheridan Way, Mississauga, Ontario, Canada L5J 2M4
Telephone: (416) 823-7381 Telex: 06-982328

CONTRACT REPORT NO. 1SQ85-00163

GOLD MILL EFFLUENT TREATMENT

UTILIZING ION EXCHANGE TECHNOLOGY

VOLUME I

DSS Contract No. 03SQ.23440-5-9121

Project No. 5152

for

Department of Supply and Services
11 Laurier St.
Hull, Quebec
K1A 0S5

October, 1986

J. L. Laird
Janet L. Laird
Project Metallurgist

M.K. Witte
President

75pp

0656A

MICROMEDIA

TABLE OF CONTENTS

VOLUME I

		PAGE
1.0	SUMMARY	1
2.0	INTRODUCTION	5
3.0	SUMMARY OF LITERATURE SURVEY	8
4.0	INDUSTRY REVIEW	12
4.1	Regulations and Guidelines	12
4.2	Discussion of Survey Results	16
4.3	Survey Conclusions	24
5.0	SUMMARY OF EXPERIMENTAL RESULTS	26
5.1	Resin Selection	28
5.2	Column I Testwork	31
5.2.1	Background	31
5.2.2	Recovery of HCN from an Acidic Regenerant Solution	34
5.2.3	Elution of Resin Loaded with Metal Cyanide Complexes	37
5.2.4	Elution Isotherms	38
5.2.5	Cyclic Adsorption/Elution Testwork	39
5.2.6	Resin Poisoning Agents	44
5.2.6.1	Adsorption/Elution Cyclic Testwork using Enriched Cyanide Waste Effluent	44
5.2.6.2	Removal of Iron Cyanide from Strong Base Resin	46
5.2.6.3	Removal of Cobalt Cyanide from Strong Base Resins	47
5.2.7	Removal of Antimony and Arsenic from Mill Effluent using Ion Exchange Resins	48
5.3	Column II - Testwork	49
5.3.1	Background	49
5.3.2	Preconditioning Step	50
5.3.3	Cyclic Testwork	51
5.3.3.1	Cyanide Recovery	52
5.3.3.2	Equilibrium Capacity - Loss of Copper from Resin	52
5.3.3.3	Loading Isotherms: Royal Barren Behaviour and Breakthrough Capacity	54

WD1

		PAGE
5.3.4	Other Forms of Amberlite IRA-400	55
5.4	Column I and Column II Operated in Series	57
5.4.1	Deportment of Co, Cu, Fe, Pb, Mo, Ni and Zn	57
5.4.2	Deportment of Sb and As	59
5.4.3	Deportment of SCN	59
5.4.4	Deportment of CN(t)	60
6.0	CONCLUSIONS AND RECOMMENDATIONS	61
7.0	REFERENCES	63

VOLUME I

LIST OF TABLES

		PAGE
TABLE 1	British Columbia, 1979 Objectives	13
TABLE 2	Northwest Territories - Site Specific Criteria	14
TABLE 3	Ontario - Guidelines and Criteria for Hemlo	15
TABLE 4	Quebec - Provincial Guidelines	16
TABLE 5	CN Destruction by Natural Degradation	17
TABLE 6	CN Destruction by Sulphur Dioxide/Air	19
TABLE 7	CN Destruction by Hydrogen Peroxide	20
TABLE 8	CN Destruction by Other Methods	21
TABLE 9	Summary of Testwork on the Recovery of HCN in Alkaline Absorbers	35
TABLE 10	Comparison of CANMET and Wittock/Lac Eluants for Recovery of Cyanide and Base Metals from Resin	38
TABLE 11	Recovery of Sb, As, Co, Hg and Mo Using a Strong Base Resin	45
TABLE 12	Elution Testwork on the Removal of Iron Cyanide Complexes from Strong Base Resins	46
TABLE 13	Cyclic Testwork: Column II	53
TABLE 14	Comparison of Cuprocyanide, Sulphate and Hydroxide Forms of IRA-400	56
TABLE 15	Deportment of All Metals, Cyanide and Thiocyanate During Two Column Cyclic Testwork	58

VOLUME II

		PAGE
	APPENDICES	
APPENDIX I	Description of the Literature	A.I.1
APPENDIX II	Analytical Procedures	A.II.1
APPENDIX III	Experimental Results and Procedures	A.III.1
A.III.1.0	Resin Selection: Barren Levels and Breakthrough and Equilibrium Capacities	A.III.2
A.III.2.0	Column I Testwork	A.III.17
A.III.2.1	Background	A.III.17
A.III.2.2	Recovery of HCN from an Acidic Regenerant Solution	A.III.21
A.III.2.3	Elution of Resin Loaded with Metal Cyanide Complexes	A.III.40
A.III.2.4	Elution Isotherms	A.III.44
A.III.2.5	Cyclic Adsorption/Elution Testwork	A.III.47
A.III.2.6	Resin Poisoning Agents	A.III.67
A.III.2.6.1	Adsorption/Elution Testwork using Enriched Cyanide Waste Effluent	A.III.67
A.III.2.6.2	Removal of Iron Cyanides from Strong Base Resins	A.III.75
A.III.2.6.3	Removal of Cobalt Cyanide from Strong Base Resins	A.III.77
A.III.2.7	Removal of Antimony and Arsenic from Mill Effluent using Ion Exchange Resins	A.III.79
A.III.3.0	Column II - Testwork	A.III.95
A.III.3.1	Background	A.III.95
A.III.3.2	Preconditioning Step	A.III.96
A.III.3.3	Cyclic Testwork - Cyanide Levels in Barrens, Breakthrough and Equilibrium Capacity and loss of Copper from Preconditioned Resin	A.III.97
A.III.3.4	Other Forms of Amberlite IRA 400	A.III.109
A.III.4.0	Column I and Column II Operated in Series	A.III.115
APPENDIX IV	Cyanide Recovery and Recycle Questionnaire	A.IV.1
APPENDIX V	References	A.V.1

VOLUME II

LIST OF TABLES

		Page
TABLE 1	Analysis of Composite Feed Samples	A.III.4
TABLE 2	Column I Effluent Analysis; Test 1	A.III.6
TABLE 3	Column I Effluent Analysis: Test 2	A.III.6
TABLE 4	Column II Effluent Analyses; Tests 1 and 2	A.III.7
TABLE 5	Column I Effluent Analysis; Test 3	A.III.10
TABLE 6	Column I Effluent Solution Analysis; Test 4	A.III.11
TABLE 7	Test 2: Recovery of HCN in Alkaline Trap	A.III.27
TABLE 8	Tests 3, 4, 5: Recovery of HCN in Alkaline Traps	A.III.30
TABLE 9	Summary of Testwork on the Recovery of HCN in Alkaline Absorbers	A.III.38
TABLE 10	Optimization of Stripping Process	A.III.41
TABLE 11	Comparison of CANMET and Witteck/Lac Effluents for Recovery of Cyanide and Base Metals from Resin	A.III.47
TABLE 12	Copper Recoveries during Cyclic Testwork, Column I	A.III.51
TABLE 13	Zinc Recoveries during Cyclic Testwork, Column I	A.III.55
TABLE 14	Nickel Recoveries during Cyclic Testwork, Column I	A.III.56
TABLE 15	Iron Recoveries during Cyclic Testwork, Column I	A.III.58
TABLE 16	Cyclic Testwork: Amount of Waste Effluent Treated Concentration of Regenerant Solution	A.III.62
TABLE 17	Cyclic Testwork using Enriched Cyanide Waste Effluent	A.III.69
TABLE 18	Removal of Sb, As, Co, Hg and Mo from Mill Effluent	A.III.73
TABLE 19	Elution Testwork on the Removal of Iron Cyanide Complexes from Strong Base Resin	A.III.76
TABLE 20	Removal of Antimony and Arsenic from Effluent: Tests 1-5	A.III.81
TABLE 21	Removal of Antimony and Arsenic from Effluent using Ion Exchange Resins: Tests 6-9	A.III.83
TABLE 22	Removal of Antimony and Arsenic from Effluent: Test 10	A.III.84
TABLE 23	Removal of Antimony and Arsenic from Effluent: Tests 11 and 12	A.III.86
TABLE 24	Removal of Antimony and Arsenic from Effluent: Tests 13-20	A.III.89

LIST OF TABLES cont.

		Page
TABLE 25	Removal of Antimony and Arsenic from Effluent: Tests 21-24	A.III.90
TABLE 26	Removal of Antimony and Arsenic from Effluent: Tests 25-29	A.III.91
TABLE 27	Removal of Antimony and Arsenic from Effleunt: Tests 30-33	A.III.93
TABLE 28	Cyclic Testwork - Column II	A.III.100
TABLE 29	Cycle I: Loading of Column II	A.III.105
TABLE 30	Cycle 5: Loading of Column II	A.III.106
TABLE 31	Cycle 6: Loading of Column II	A.III.107
TABLE 32	Comparison of Breakthrough and Equilibrium Loading Capacities for "CuCN", Sulphate and Hydroxide Forms of Amberlite IRA-400	A.III.113
TABLE 33	Comparison of Breakthrough and Equilibrium Capacity	A.III.114
TABLE 34	Cyclic Testwork: Column I Loading Data for Cycle I	A.III.117
TABLE 35	Cyclic Testwork: Column I Loading Data for Cycle II	A.III.118
TABLE 36	Cyclic Testwork: Column II Loading Data for Cycle I	A.III.119
TABLE 37	Cyclic Testwork: Column II Loading Data for Cycle II	A.III.120
TABLE 38	Resin Analyses after Two Loading/Stripping Cycles	A.III.121

VOLUME II

LIST OF FIGURES

		PAGE
FIGURE 1	Test 3: Column 1 Loading Isotherms	A.III.12
FIGURE 2	Test 4: Column 1 Loading Isotherms	A.III.13
FIGURE 3	Test 3: Column 2 Loading Isotherms	A.III.15
FIGURE 4	Test 4: Column 2 Loading Isotherms	A.III.16
FIGURE 5	Apparatus used for Test 1 of HCN Recovery Testwork	A.III.22
FIGURE 6	Relative Amounts of HCN and CN as a Function of pH	A.III.24
FIGURE 7	Apparatus used for Test 2 of HCN Recovery Work	A.III.26
FIGURE 8	Apparatus used for HCN Recovery Test 3, 4 and 5	A.III.31
FIGURE 9	Recovery of HCN in Alkaline Traps - Tests 3, 4 and 5	A.III.33
FIGURE 10	Apparatus used for HCN Recovery - Test 6	A.III.35
FIGURE 11	Test 6: Amount of Cyanide Recovered in Trap 1 versus Time	A.III.37
FIGURE 12	Apparatus used for Stripping Tests 1 to 3.	A.III.42
FIGURE 13	Stripping Isotherms for Test 1 using 1% Sulphuric Acid Eluant	A.III.45
FIGURE 14	Stripping Isotherms for Test 2 using Witteck/Lac Eluant	A.III.46
FIGURE 15	Stripping Isotherms for Copper and Zinc	A.III.48
FIGURE 16	Cycle 1 Recovery of Cyanide in Caustic Trap	A.III.60
FIGURE 17	Cobalt Recovery from Resin using $NH_4SCN/NaOH$	A.III.78
FIGURE 18	Loading Isotherm for Cycle 1 of Column II Testwork	A.III.102
FIGURE 19	Loading Isotherm for Cycle 5 of Column II Testwork	A.III.103
FIGURE 20	Loading Isotherm for Cycle 6 of Column II Testwork	A.III.104
FIGURE 21	Loading Isotherm for Sulphate, Hydroxide and Cuprocyanide Forms of IRA-400	A.III.111
FIGURE 22	Loading Isotherms for Sulphate, Hydroxide and Cuprocyanide Forms of IRA-400 (semi-logarithmic)	A.III.112

ACKNOWLEDGEMENT

This report is based on a project carried out by Witteck Development Inc. with the collaboration of CANMET. Witteck Development Inc. acknowledges the contributions of the CANMET staff and many Canadian gold mines/mill staff for their support and assistance.

1.0 SUMMARY

The following paper reports on the results of Phase I of a three-phase test and feasibility study entitled "Gold Mill Effluent Treatment Utilizing Ion Exchange Technology" (DSS Contract 03SQ.23440-5-9121).

The objectives of Phase I were:

1. Survey the gold milling industry to assess the current status of effluent treatment and to determine the need for new technology.

2. Complete a literature search to assess the status of ion exchange technology and any advances which have taken place since the original CANMET studies.

3. Complete research and development testwork to confirm the CANMET ion exchange technology and to try to solve the remaining process problems with the CANMET two column system.

4. Review and select the best ion exchange unit processes available, then combine these technologies to produce a complete flowsheet. Loading and elution data, and bench scale continuous studies were to be undertaken to compare this new technology against the CANMET technology.

The response to the industry survey indicated a larger effluent treatment concern with operations utilizing carbon-in-pulp circuits than with operations which use zinc precipitation circuits. This is due primarily to the latter's ability to recycle zinc precipitation barrens within the plant, and therefore having to discharge only a portion from the mill.

WD1

Of the 21 respondents to the questionnaire which utilized some method of effluent treatment, sixty-seven percent utilized natural degradation, nineteen percent used INCO's SO_2/air process, and fourteen percent utilized hydrogen peroxide. None of the respondents are currently using the alkaline chlorination process.

Most operations indicated that a significant cost saving could result from the recovery and recycle of cyanide. Any new technology which could incorporate cyanide recycle with effluent treatment might be very attractive economically. This would have to be evaluated in terms of operational cost savings and payback of capital costs.

The results of the survey indicated clearly that the market ability of the ion exchange technology would have to be based solely on economics. All of the effluent treatment processes considered have the abiilty to produce environmentally acceptable effluents.

The literature survey indicated that interest in the use of ion exchange technology for cyanide recovery has been very limited since the 1960's and 1970's. Since the original CANMET work, weak base resins have been investigated with limited success, and so has the use of complexation reagents to recover the free cyanide as a metal cyanide complex. While more recent workers have investigated the use of ion exchange for the recovery of cyanide from electroplating wastes, no major improvements have been made to the two column ion exchange technology developed by CANMET. However, other workers (19) have developed novel technology using a single column system for the recovery of cyanide from gold mill effluent.

The results of the current test program on the CANMET two column system for the recovery of both the metal complexed cyanides (column I) and free cyanide (column II) are summarized below:

- Greater than 90% of the cyanide present in the waste effluent solution can be recovered as a concentrated NaCN solution

- A portion of the column I effluent, which contains only lime, free cyanide and thiocyanate can be used as the alkaline trap for cyanide recovery. The effluent trap solution can be enriched to at least 10 g/L CN and recycled to the mill.

- Acceptable barren effluent is produced by the two column process [$<$0.01 ppm Cu; $<$0.02 ppm Fe; $<$0.01 ppm Ni, $<$0.01 ppm Zn; $<$0.05 ppm Co, $<$0.05 ppm Pb; $<$ 1 ppm SCN, $<$ 1 ppm CN(t)]. While the leakage of cyanide from the second column did exceed the 0.1 ppm CN(t) target, the 1 ppm target currently recommended by most provincial governments is achieved easily. A more serious effluent problem would be the leakage of arsenic and antimony in the column effluent; neither of which are adsorbed efficiently by the resin. As with the destructive processes, arsenic precipitation using ferric iron would have to be used in conjunction with the ion exchange technology.

- The elution procedure utilized by CANMET (12) for the removal of base metal cyanide complexes from column I has been improved. It has been shown that whereas the CANMET procedure does not fully recover copper cyanide from the resin, a procedure developed in 1981 by Witteck in collaboration with Lac Minerals Ltd. recovers copper, nickel, zinc and cyanide efficiently from the resin.

0656A

WD1

- Cyclic testwork on the column I technology indicated no build-up of copper, nickel nor zinc on the resin. However, iron and cobalt were identified as resin poisoning agents.

- A number of loading tests were carried out to find a resin and conditions under which antimony and arsenic could be removed from the effluent using ion exchange technology. Unfortunately, loading efficiencies were poor under a wide variety of conditions.

- The leakage of cyanide from column II during adsorption, which was identified by Gilmore (12) as a "royal barren", was observed during the present testwork. It was determined that this behaviour is not a first cycle phenomena. Although a target value of 0.1 ppm CN(t) was not achieved using the two column system, 1 ppm CN(t) is possible.

- The cuprocyanide form of the resin was compared to the sulphate and hydroxide forms for column II. The sulphate form displayed the lowest loading capacities to breakthrough. The cuprocyanide form displayed higher equilibrium capacity (32 mg CN/mL resin) than did the hydroxide form (25 mg CN/mL resin). However, while the cuprocyanide form did not achieve the target level of 0.1 ppm CN(t) in the column effluent, the hydroxide form did. The loading here was to 15.3 mg CN/mL resin before breakthrough.

2.0 INTRODUCTION

Prior to 1983, conventional effluent treatment technology for Canadian gold mills consisted primarily of natural degradation and alkaline chlorination. The alkaline chlorination process was chosen over other experimental methods tested in the 1970's because laboratory studies indicated that acceptable effluent standards could be met and that the technology had a low capital cost.

As the process was installed by milling operators, various problems arose with the technology. These problems ranged from high chlorine consumption due to chlorination of the thiocyanates prior to complexing of the cyanides, to operational problems such as the formation of cyanogen chloride.

In more recent years, two new oxidative processes have gained popularity: the Inco SO_2/air and the hydrogen peroxide destructive processes. While neither of these methods quantitatively oxidize the cyanide present as iron cyanide complexes, the SO_2/air method does result in removal of iron cyanide by precipitation as dimetal cyanide complexes. For all three of the above processes, the precipitated base metals report to the tailings impoundment area along with the treated effluent stream.

The recent surge in gold milling in Canada as typified by the three Hemlo gold operations, has resulted in renewed interest in the long term environmental implication of the various cyanide destruction methods. Also of interest is the potential for non-destructive removal of cyanide.

In the 1970's, CANMET carried out a thorough investigation into all the possible treatment technologies. The results of their findings were that ion exchange technology had the greatest chance of succeeding as a non-destructive method for the recovery and recycle of cyanide from waste gold mill effluent solutions. Ion exchange has the potential to remove both the base metal and cyanide species from solution. Furthermore, the cyanide may be recovered in a reusable form and no byproducts of cyanide destruction (such as cyanate) are produced and released to the environment.

The effluent treated by ion exchange could be more acceptable environmentally than that produced by a destructive process, however this was never proven. Extensive work was completed by CANMET on the ion exchange technology, but because of inherent process difficulties and the more attractive economics of alkaline chlorination, the process technology was not further developed. At the time, mill operators felt that alkaline chlorination was the method of choice because it was not capital intensive and it appeared to solve the problems.

This study, funded under DSS Contract No. 03SQ.23440-5-9121, commenced in July of 1985. The original proposal outlined a three phase test and feasibility program to assess the current status of effluent treatment in the gold milling industry and to further study the use of ion exchange as a potential process for milling operators. The program had been broken down into the following phases:

Phase I - Literature review, industry survey, benchscale evaluation of CANMET's technology and further development of the ion exchange technology for cyanide effluent treatment.

Phase II - Pilot plant testwork to confirm the technology and to demonstrate to industry that the technology is feasible commercially.

Phase III- An economic feasibility study to compare the overall capital and operating costs for the newly developed ion exchange technology to those for cyanide destruction using oxidative technologies.

The work for Phase I has been completed and is reported herein.

The testwork procedures and detailed results have been placed in appendices allowing the text to contain summarized data and comment.

Conclusions and recommendations have been made to further technological progress in the area of effluent treatment.

3.0 SUMMARY OF LITERATURE SURVEY

Prior to commencing further research and development work on ion exchange recovery of cyanide, a thorough literature survey was completed. Appendix I provides a detailed description of each paper reviewed. The reference list is provided in Section 8.0. Ion exchange of cyanide and cyanide complexes has been studied for over 30 years. The following is a summary of the prior work.

Burstall et al (1), first investigated the use of ion exchange for the recovery of metal cyanide complexes from mill effluent solutions. His work focused on the recovery of aurocyanide, as well as all base metal cyanide complexes, using a strong base anionic exchange resin (Amberlite IRA-400). He proposed a complicated four stage selective elution process for recovery of gold and the various base metals from the resin. This initial work did not address the problem of recovering free or uncomplexed cyanide from solution.

In 1959, Goldblatt (2) published the work which acted as a forerunner to the present study. Starting with gold barren solution, Goldblatt used a primary column containing the same resin which Burstall had used (Amberlite IRA-400, sulphate form), to remove base metal cyanide complexes from the effluent solution. A secondary column was added for the removal of uncomplexed cyanide. This second column also contained Amberlite IRA-400 resin in the sulphate form, but the resin had been preconditioned with a solution of cuprocyanide. Prior to loading, the preconditioned resin is washed with 1% H_2SO_4, in order to remove any available cyanide from the resin, leaving the resin in the "CuCN" form. During adsorption, the free cyanide was recovered from the waste effluent by converting the resin from the CuCN form to the $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ or $Cu(CN)_4^{3-}$ form.

After adsorption, both the primary and secondary columns were eluted with 1% sulphuric acid. The primary column eluate, containing metal sulphates and HCN was passed through a third column containing cationic exchange resin, which removed the base metals from solution. The effluent from the third (cationic) column contained only sulphuric acid and HCN and could be recycled to the mill, along with the eluate from the second column. The third column was eluted using 10% NaCl. This eluate contained the base metals, and reported to the tailings area.

After this, weak base resins were investigated by various authors (4, 5, 6, 7, 8). While weak base resins have the advantage of being readily eluted by pH control (NaOH, pH > 10), thereby eliminating the need for selective elution, there are many disadvantages. The feed solution pH must be near or below the apparent pKa of the resin for efficient loading. For most commercially available weak base resins, this means that the feed solutions must be adjusted to pH 8 or below. This is not practical for gold mill effluent, both from a cost point of view (cost of H_2SO_4 addition; removal of gypsum formed), and from a safety aspect (decomposition of most metal cyanide complexes and volatilization of HCN at pH less than 9). Furthermore, elution with NaOH produces an eluate containing the same amount of cyanide, and the same form of the cyanide (base metal complexes) as was in the original stream; the solution has been concentrated only. This solution is of limited use in gold mills, where free cyanide is desirable for recycling.

While Goldblatt proposed the use of a preconditioned resin for the adsorption of free cyanide, various subsequent workers (4, 6, 7, 9, 10, 11) proposed the addition of base metals to the waste effluent to complex the free cyanide, thereby allowing for the removal of all cyanide on a single ion exchange column.

0656A

WDI

The primary problem encountered with this approach, was the requirement of the stoichiometric addition of the metal ion to complex the free cyanide. The addition of insufficient metal allows the leakage of free cyanide from the column during the adsorption cycle; the addition of excess metal produces nonionic metal cyanide complexes, which do not adsorb on to the anionic resins, and which may precipitate out of solution, either in the resin bed, or in the column effluent.

Therefore, the complexation of free cyanide approach required process control for the stoichiometric addition of a metal ion to a stream which fluctuates in free cyanide concentration. This problem has yet to be solved satisfactorily.

At this stage (@ 1975) the use of strong base resins was reinvestigated by a variety of workers (9, 10, 11, 12, 13, 15, 16). Complexation of free cyanide using ferrous ion was studied (9, 10) since ferrocyanide is stable with respect to reaction with excess metal ions, and therefore does not produce nonionic metal cyanide complexes. The excess ferrous ion is simply precipitated and recovered quantitatively as ferrous hydroxide. Although a 15% NaCl solution was used to remove the ferrocyanide complex from the resin, other base metal cyanide complexes which would be present in typical gold mill effluent, would require a multielution process to fully strip the resin.

In 1976, Gilmore (12) at CANMET reinvestigated Goldblatt's two column system for removal of base metal cyanide complexes and free cyanide from gold mill effluent. Six different gold mill effluents were tested.

In summary, Gilmore found that although the primary column performed well at removal of base metal cyanides, the secondary column leaked cyanide during the initial stages of the adsorption cycle. Further testwork indicated that two sulphate columns operating in series would be more effective in attaining an effluent containing less than 0.1 ppm CN(t), than the two resin forms first proposed by Goldblatt (2).

In a subsequent paper (13), Gilmore at CANMET reported the results of a pilot plant study of the process, which demonstrated the ability of the technology to decrease cyanide concentrations in gold mill effluent to less than 0.1 ppm CN(t), and to remove base metals to acceptable levels.

Subsequent workers have investigated the use of ion exchange for the recovery of cyanide from electroplating wastes. However, there has been no further work completed on the two column ion exchange technology first developed by Goldblatt, and improved upon by CANMET.

Recent studies conducted by Witte et al (19) at Witteck Development Inc. have investigated the use of a novel single column ion exchange system. While this system currently is being pilot tested by Lac Minerals at La Mine Doyon near Rouyn Quebec, and developmental work is being carried out for Gordex Minerals in St. John, New Brunswick, little information is available to date due to confidentiality agreements between Witteck Development and Lac Minerals and Gordex Minerals.

4.0 INDUSTRY REVIEW

Prior to completing any further testwork on ion exchange, it was felt that a complete up-to-date assessment of industry practice was needed as a basis to determine if ion exchange technology could be utilized by industry. Important factors for investigation included plant cyanide consumption and the overall need for a more efficient effluent treatment system.

To complete this review, 47 gold mining operations, principally in the provinces of Ontario and Quebec and a few in British Columbia, were asked to respond to a questionnaire. A total of 27 responses were received. Of these 27, 6 operations produced a flotation concentrate and did not cyanide the concentrate.

The 21 relevant operations use SO_2, peroxide, or natural degradation. A copy of the questionnaire is provided in Appendix IV.

4.1 Regulations and Guidelines

No federal guidelines exist for water quality for discharge to the environment from gold mill impoundment areas. The regulations provided in the "Metal Mining Liquid Effluent Regulations and Guidelines" do not apply to gold mines and do not provide criteria for cyanide, thiocyanate or cyanate. However, the guidelines given for base metals are considered when licences are granted to mines in the North West Territories.

Most provinces set guidelines or objectives. In some cases, only site specific criteria are available. The three provinces of primary interest, British Columbia, Ontario and Quebec, as well as the North West Territories are discussed below.

BRITISH COLUMBIA*

In 1979, a range of provincial objectives for maximum dischargeable levels was published. Since this time, some mines have been allowed to exceed the 1979 objectives. Regulations and licences in B.C. are site specific, guidelines however, are being developed for discharge into specific rivers.

The 1979 objectives, as well as one of the site specific criteria are provided below.

Table 1

BRITISH COLUMBIA, 1979 OBJECTIVES

	1979 Objectives ppm	North Air ppm
CN(t)	0.1 to 0.5	0.1
CN(WAD)	Under Consideration	-
SCN	-	-
CNO	-	-
As(III)	0.05 to 0.25	-
As(TD)**	0.10 to 1.0	-
Zn(TD)	0.20 to 1.0	0.5
Cu(TD)	-	0.5
Fe	-	0.3
Pb	-	0.05

* Information provided by Perri Meihling

** TD - Total Dissolved

0656A

NORTHWEST TERRITORIES

As mentioned above, the Northwest Territories, being under federal jurisdiction, use the 1977 "Metal Mining Liquid Effluent Regulations and Guidelines" as a guideline for base metals. Licences, however, are site specific. A few of the criteria for individual mines are listed below.

Table 2

NORTHWEST TERRITORIES - SITE SPECIFIC CRITERIA

	Cominco Con, ppm		Giant Yellowknife, ppm	
	Maximum Arithmetic Mean	Maximum Grab Sample	Maximum Arithmetic Mean	Maximum Grab Sample
CN(t)	1.5	3.0	1.5	3.0
CN(WAD)	0.4	0.8	-	-
As	0.5	1.0	0.8	1.6
Sb	-	-	-	-
Zn	0.5	1.0	0.5	1.0
Cu	0.3	0.6	0.5	1.0

	Giant Salmita, ppm		Culaton, ppm	
	Maximum Arithmetic Mean	Maximum Grab Sample	Maximum Arithmetic Mean	Maximum Grab Sample
CN(t)	-	-	2.0	4.0
CN(WAD)	-	-	-	-
As	0.2	0.4	0.5	1.0
Sb	-	-	-	-
Zn	0.3	0.6	0.5	1.0
Cu	0.1	0.2	0.3	0.6

* Information provided by Dave Sutherland, Environmental Protection Service, Yellowknife

0656A

ONTARIO*

Unlike Quebec, Ontario licences are site-specific with a general guideline that requires minimum treatment of the effluent from the mining operation.

The October 1981 guidelines as well as one of the specific site criteria are presented below.

Table 3

ONTARIO - GUIDELINES AND CRITERIA FOR HEMLO

	1981 Guideline ppm*	Hemlo ppm**
CN(t)	2	2
Sb	-	1
As	0.5	0.5
Cu	1	1
Fe	1	1
Mo	1	1
Ni	1	1
Pb	1	1
Zn	1	1
(Zn + Pb + Ni + Cu)	1	1
NH_3	10	10 (no-ionized)
NO_3	-	1
Suspeded Solids	15	15

Information * obtained from Ministry of Environment, Guidelines for Environmental Control in the Ontario Mineral Industry - October 1, 1981.

** provided by Lac Minerals, Hemlo

0656A

QUEBEC

As opposed to B.C. and Ontario, Quebec licences are not site specific. Provincial guidelines have been published; regulations, however, do not exist. The provincial guidelines are provided below.

Table 4

QUEBEC - PROVINCIAL GUIDELINES

	Quebec Guidelines ppm
CN(t)	1.5
CN(WAD)	0.10
As	0.5
Sb	-
Cu	0.15
Fe	3.0
Zn	0.5
Ni	0.5

* Information obtained from Government of Quebec, Ministry of Industries - Directive #019.

4.2 Discussion of Survey Results

A 60% response was received to the questionnaire for information on the treatment of gold mill effluents. Of the 21 respondents who actually use cyanide in their circuits, fourteen (63.6%) rely on natural degradation to obtain their effluent. Four operations (18.2%) use sulphur dioxide/air and three operations (13.6%) use hydrogen peroxide. One mine, La Mine Doyon, is currently piloting ion exchange to remove and recover base metals and recycle cyanide contained in an effluent bleed.

Tables 5 to 8 summarize the results of the survey for operations which use natural degradation, sulfur dioxide/air, hydrogen peroxide and other methods, respectively.

CN DESTRUCTION BY NATURAL DEGRADATION

Table 5

Company	Process Details: Tonnage (tpd)	NaCN Cons'n kg/ton	Effl't Flow (M /hr)	Recy'l Flow (M /hr)	Au Rec'y Process	Effluent Chemical Details (ppm): Mill Discharge CN	CN	SCN	Cu	Fe	Zn	Ni	As	Effluent Discharged to Environment CN	CN	SCN	Cu	Fe	Zn	Ni	As
A	2500	*	-	12	Zn ppt	no effluent from cyanide dam															
B	2500	*	55	12	Zn ppt	-	-	-	-	-	-	-	-	0.22	-	-	0.85	0.28	0.15	-	-
C**	1100	0.75	379	small amount	Zn ppt	4.0	4.0	-	0.1	-	0.08	0.1	-	-	-	-	-	-	-	-	-
D	3000	0.25	375	0	Zn ppt	60-90	-	-	-	-	-	-	-	0.11	low	-	0.34	0.34	0.15	0.44	-
E	1400	0.20	N/	57	Zn ppt	-	-	-	-	-	-	-	-	0.456	0.4	-	0.5	0.8	-	-	-
F***	175	0.82	24	-	Zn ppt	-	-	-	-	-	-	-	-	0.081	-	-	0.085	-	0.208	0.04	1.54
G	500	0.5	-	53	Zn	- ppt	-	-	-	-	-	-	-	0.12	-	-	0.27	0.28	0.03	0.12	0.01
H	1100	1.25	125	50	Zn ppt	5.88	-	-	3.33	0.98	0.28	2.95	3.39	0.17	-	-	1.60	1.41	0.17	1.33	2.20

Note: All Numbers are those reported by company representatives. Check analysis have not been completed as part of this study. Dashes indicate information not available from company.

* Cyanidation of flotation concentrate only; tonnage not available.

** Effluent to barren holding pond which is drained to the tailing pond in summer.

*** Effluent held in containment pond with area sufficient for evaporation.

CN DESTRUCTION BY NATURAL DEGRADATION

Table 5, cont'd

Company	Process Details: Ton-nage (tpd)	NaCN Cons'n kg/ton	Effl't Flow (M³/hr)	Recy'l Flow (M³/hr)	Au Rec'y Pro-cess	Effluent Chemical Details (ppm): Mill Discharge CN_T	CN_F	SCN	Cu	Fe	Zn	Ni	As	Effluent Discharged to Environment CN_T	CN_F	SCN	Cu	Fe	Zn	Ni	As
I	1800	1.15	120	34	Zn ppt	160	120	-	3-5	3-15	22	-	-	0.06	0.01	-	0.01	2.0	0.2	-	0.5
J	750	1.)	66		Zn ppt	79.5	NA	NA	9.8	NA	4.0	3.05	3.18	0.4	-	-	0.62	-	0.22	0.28	0.62
K	1200	1.)	48	35	CIP	5-6	4-5	<1	1.5	4.8	0.3	0.05		-	-	-	-	-	-	-	-
L	1950	0.3	76	-	Zn ppt	149	133	-	19.2	0.11	8.55	-	-	2.17	1.64	-	1.88	1.34	0.06	-	-
M*	1000	1.0	104	-	CIP	400	-	-	7.0	3.0	0.35	-	-	-	..	-	-	-	-	-	-
N	2700	NA	-	-	CIP	-	-	-	-	-	-	-	-	-	..	-	-	-	-	-	-

Note: All Numbers are those reported by company representatives. Check analysis have not been completed as part of this study.

* Effluent contained in ponds; no discharge yet.

0691A

CN DESTRUCTION BY SULPHUR DIOXIDE/AIR

Table 6

Company	Process Details: Tonnage (tpd)	NaCN Cons'n kg/ton	Effl't Flow (M /hr)	Recy'l Flow (M /hr)	Au Rec'y Process	Effluent Chemical Details (ppm): Mill Discharge CN	CN	SCN	Cu	Fe	Zn	Ni	As	Effluent Discharged to Environment CN	CN	SCN	Cu	Fe	Zn	Ni	As
O	400	0.88	37	47	Zn ppt	90	68	168	55	0.18	4.10	-	-	0.15	0.25	80	0.75	0.53	0.03	-	-
P	5500	-	500	416	CIP	120	60	350	60	5	2	-	-	-	-	-	-	-	-	-	-
Q*	600	0.30	6-12	~ 170	Zn ppt	— Solution treated before leaving mill —								0.7	-	82	1.2	0.26	0.23	-	-
P	1500	0.25	7	79	Zn ppt	11	11	32	7	0.4	-	-	-	0.72	(.086	-	0.16	-	-	-	-

Note: All Numbers are those reported by company representatives. Check analysis have not been completed as part of this study. Dashes indicate information not available from company.

* Analysis given refers to discharge from CN destruction circuit.

0691A

CN DESTRUCTION BY HYDROGEN PEROXIDE

Table 7

Company	Process Details: Tonnage (tpd)	NaCN Cons'n kg/ton	Effl't Flow (M /hr)	Recy'l Flow (M /hr)	Au Rec'y Process	Effluent Chemical Details (ppm): Mill Discharge CN	CN	SCN	Cu	Fe	Zn	Ni	As	Effluent Discharged to Environment CN	CN	SCN	Cu	Fe	Zn	Ni	As
S	1000	0.8	27	112	CIP	150-300	104-270	11-160	3-8	5-8	0.5-1.0	-	-	0.4	<0.05	0.5	0.01 .5	0.01 .7	<0.005	-	.
T *	12	-	0.8	0.8	Carbon Columns	2000	200	5000	1200	20	< 0	-	-	0.02	-	1	0.008	0.026	0.006		0.035
W	3000	-	-	-	CIP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

Note: All Numbers are those reported by company representatives. Check analysis have not been completed as part of this study.

Dashes indicate information not available from company.

* Cyanide also used in flotation circuit

0691A

CN DESTRUCTION BY OTHER METHODS

Table 8

Company	Process Details: Tonnage (tpd)	NaCN Cons'n kg/ton	Effl't Flow (M /hr)	Recy'l Flow (M /hr)	Au Rec'y Process	Effluent Chemical Details (ppm): Mill Discharge CN	CN	SCN	Cu	Fe	Zn	Ni	As	Effluent Discharged to Environment CN	CN	SCN	Cu	Fe	Zn	Ni	As
V *	1500	0.63	5	70	Zn ppt	50	37	-	15	2	2	-	-	0.4	0.05	-	4	5	0.10	-	-

Note: All Numbers are those reported by company representatives. Check analysis have not been completed as part of this study. Dashes indicate information not available from company.

* Testing Ion Exchange on pilot scale - numbers represent normal milling conditions without IX treatment.

0691A

The survey also indicated that out of the 21 applicable operations, 15 use zinc precipitation as a method of gold recovery and 6 use carbon-in-pulp (CIP) or carbon columns. Most of those operations using zinc precipitation have the ability to recycle barren within the plant and therefore discharge only a portion of their mill effluent. CIP circuits, however, must discharge all effluent and recycle water to the mill must be returned from diluted (with rain water run-off) tailing water. Therefore, effluent treatment appears to be a more serious problem with operations running CIP circuits than with operations running zinc precipitation circuits. At least one operation, Kiena, who chose not to respond to the survey, is now filtering CIP tailings prior to discharge in order to reduce treatment costs and to create the ability to recycle barrens directly.

Since guidelines and specifications for environmental control vary from province to province and site to site, it is impossible to determine or assess which operations are in compliance with their operating permits. The survey has shown, however, that the effluent discharged to the environment from most operations is quite acceptable and that the operators are seriously trying to meet guidelines. Natural degradation appears to be an acceptable method of dealing with the bulk of the cyanide complexes but if very low levels of total cyanide, metals, arsenic and antimony must be met, some tail-end polishing steps to reduce these levels must be undertaken.

Where chemical treatment is applied to the mill effluent or tailings management pond overflow, the INCO SO_2 process introducing sulphur dioxide and air into the tailings effluent or slurry is the most popular. This technology seems to have displaced alkaline chlorination which was used at Carolyn Mines but presently is not used by any of the respondents to the questionnaire.

0656A

The hydrogen peroxide technology which is relatively new to the Canadian industry is used by two of the Hemlo operations, Teck-Corona and Noranda, to obtain an environmentally acceptable effluent. The fate of this technology is unknown at this point but the peroxide route appears to easily produce respectable effluents.

Arsenic and antimony in the tailing effluent appears to be one of the more serious problems that the mine operators have to handle. Arsenic and antimony do not respond to SO_2/air nor to H_2O_2 treatment. In cases where the levels are high, a secondary step which involves ferric iron treatment must be undertaken. This process step results in a high reagent cost and a difficult precipitate to handle and solution to clarify.

A serious problem, evident from the survey and after conversations with the milling operators, is the operations lack of expertise to develop and procure on a consistent basis, good analytical data for the monitoring of cyanide complexes in their discharge. Most of the operations send their cyanide analyses to an outside laboratory, some complete CN(t) internally and send out CNO and SCN. Many operations have never assayed their solutions for SCN and CNO. With operations sending their analyses out, proper stabilization of the samples is questionable.

Most operations stated on their response that a significant operating cost savings could be experienced by recycling cyanide. Any new technology for cyanide recycle would be evaluated on the basis of savings in operating costs and payback of capital costs. Verbal conversations with operators indicated that a process which allowed for cyanide recycle as well as effluent treatment would be welcomed by the industry but would only be attractive on an economic basis.

0656A

WD1

4.3 Survey Conclusions

As a result of conducting the survey the following conclusions may be made:

1. In general, the response to the questionnaire was good with 60% of all gold milling operators responding.

2. Based on the response, it appears that operators running zinc preciptation circuits have an easier time dealing with their effluent since internal mill recycle commonly is practiced.

3. Those operations experiencing effluent problems seem to vary from season to season during the year. Many of the operators feel that the antimony/arsenic problems are more severe than the cyanide problems since natural degradation will eventually take care of the cyanide.

4. Natural degradation is by far the most common practice among gold milling operators. SO_2/air has gained popularity as the most popular chemical treatment method. Peroxide technology is new and is practiced only by a couple of the new operators.

5. Cyanide recycle, with the inherent savings, was noted as a more important objective than effluent treatment.

6. All operations felt that new process technology to recycle cyanide and help control effluent would be welcome, however, the bottom line was economics.

Given these conclusions, development of the ion exchange technology continued but much more emphasis was placed on cyanide recycle. Scrubber efficiency and overall process efficiency became a priority during the development.

Also, it is evident that the marketability of any new technology in this area will be based solely on economics. SO_2/air, H_2O_2 as well as ion exchange all have the ability to generate acceptable effluent levels. Therefore, the fate of ion exchange will be based on process cost savings.

0656A

WD1

5.0 SUMMARY OF EXPERIMENTAL RESULTS

The objective of the continued research and development on the cyanide ion exchange recovery process was to continue the study of the two column CANMET system to alleviate process problems and establish possible design criteria. The testwork on the two column system was subdivided in four general areas. In the first section, Section 5.1, the results of the initial resin selection testwork are summarized. A comparison of resins was made on the basis of barren levels and breakthrough and equilibrium capacities for column I and column II. After the initial resin selection, the operation of each column of the two column system was investigated separately.

The results of the testwork performed on column I, for the removal of base metal cyanide complexes from effluent solution, are summarized in Section 5.2. This section describes the results of the continued investigation into stripping procedures, the percent cyanide recoverable in various types of alkaline traps, cyclic testwork involving twenty adsorption/elution cycles, the results of an investigation into potential resin poisoning agents, and the results of an investigation into the removal of arsenic and antimony using ion exchange resin.

The results of the analogous program for column II, for the removal of uncomplexed or free cyanide from mill effluent, are summarized in Section 5.3. This section includes the results of six adsorption/elution cycles, including barren levels, breakthrough capacities and loading isotherms, a reinvestigation into the preconditioning step as well as an investigation into the frequency of reconditioning the cuprocyanide form of the resin. In addition, testwork was performed on other forms of anionic exchange resins to determine if there is a form better able to remove free cyanide from gold mill effluent.

Finally, the two columns were coupled and operated in series during the last phase of the testwork. These results are summarized in Section 5.4. All elements present in the feed effluent were followed during a two cycle study of the two columns operating in series.

The detailed experimental procedures and results are provided in Appendix III. The following is a summary of the results.

5.1 Resin Selection

During preliminary testwork, two resins were investigated for their ability to remove both the base metal cyanide complexes (column I) and the free or uncomplexed cyanide (column II) from gold mill effluent solution. The two resins tested were both strong base anionic exchange resins. Weak base resins were not investigated due to their lower loading capacities at the pH levels typical of cyanide bearing waste effluent (pH 9 to 11.5).

The gel resin first utilized by Goldblatt (2) and later studied by Gilmore (12) was tested (Amberlite IRA-400), along with a macroporous strong base anionic exchange resin, Lewatit MP-500. It was anticipated that the two resins might display similar loading capacities and base levels, but that the macroporous resin might display a higher degree of physical strength. For column I, the resins were converted to the sulphate form. For column II, the resins were converted to the sulphate form and then preconditioned with a solution of copper cyanide, according to the procedure described by Goldblatt (2).

Each resin was studied using two authentic mill effluent solutions. Therefore, four tests were carried out in total. For each test, the two columns were operated in series, with the column I effluent reporting directly to column II. Sampling was carried out between the two columns and after column II. Since the primary function of column I is to remove base metals from the waste effluent, the column I effluent samples were assayed for Cu, Fe, Ni and Zn. Column II samples were assayed for CN(t) and Cu. Copper was included to determine if leakage of copper from the cuprocyanide preconditioned resin may present a problem with respect to environmental guidelines. The details of the experimental procedures and the results obtained are provided in Appendix III Section 1.0.

0656A

For the first two tests, using effluent B [67 ppm Cu; 15 ppm Fe; 47 ppm Ni; 63 ppm Zn; 636 ppm CN(t)], adsorption was terminated when metals broke through the primary column (greater than 0.1 ppm). For both of the resins, this occurred after 70 bed volumes of effluent had passed through the two columns. Breakthrough capacities were (mg/mL resin): Cu, 4.7; Fe, 1; Ni, 3.3; and Zn, 4.4. Therefore, the two resins were found to be indistinguisnable with respect to breakthrough capacities for column I.

Samples of the column II effluent indicated that a composite of the first 65 bed volumes would easily attain the target level of less than 0.1 mg/L CN(t), for either the IRA-400 or MP-500 resin. However, the IRA-400 displayed slightly better breakthrough capacities, reaching the 1 mg/L CN(t) by 74 bed volumes. At this stage the MP-500 resin had already leaked cyanide to 40 mg/L.

With respect to copper leaking from column II during loading, both resins leaked copper in excess of the proposed guideline for copper quoted by Gilmore (12), of 0.3 ppm Cu. At this stage in the testwork, it appeared that with respect to column II operations, leakage of copper from the preconditioned resin might present more of a problem than leakage of cyanide. It was decided, therefore, to investigate fully the copper levels in the column II effluent throughout the remainder of the test program.

For the second two tests using effluent A [222 ppm Cu; approximately 4 ppm Fe; 5 ppm Ni; 126 ppm Zn and approximately 477 ppm CN(t)], adsorption was continued until full equilibrium capacity was attained for at least one metal, in this case copper. This occurred after 140 bed volumes for both the IRA-400 resin (test 3) and the MP-500 resin (test 4).

At this stage, loadings for the two resins were: (mg/mL resin)

	Cu	Fe	Ni	Zn
IRA-400	23.4	0.3	0.6	15.1
MP-500	13.7	0.2	0.3	4.9

Furthermore, breakthrough occurred at different stages for the two resins. Copper breakthrough occurred at 90 bed volumes for IRA-400, and before 20 bed volumes for MP-500.

The loading isotherms for column II, for tests 3 and 4 were similar (see Appendix III, Section 1.0). Both resins allowed the leakage of cyanide (approximately 1 ppm) during the first 14 to 24 bed volumes. The cyanide levels in the column effluent then decreased to below (0.05 mg/L CN(t) for MP-500) or near (0.25 mg/L CN(t) for IRA-400) the 0.1 mg/L target briefly after 48 bed volumes, before breakthrough.

The comparison of the two resins, IRA-400 and MP-500, using two different mill effluents served to indicate that the best resin for a mill will be site-specific. In many cases, the macroporous resin behaves comparably to the gel resin, and may be less subject to attrition. Both resins were included in the remainder of the testwork.

5.2 Column I Testwork

After the resin selection testwork described above, the two columns were tested separately. The initial testwork had provided adsorption data for column I, including barren levels, breakthrough and equilibrium capacities, as well as loading isotherms. Therefore, the further testwork carried out on column I began with an investigation into the elution operation.

Prior work conducted at Witteck had indicated that the sulphuric acid strip recommended by Gilmore (12) for desorption of the primary column would not elute copper efficiently from the resin. Therefore, a reinvestigation of the elution operation was undertaken.

5.2.1 Background

In the 1976 CANMET report (12) the loaded primary column was desorbed by a downflow of a 1% H_2SO_4 solution.

$$(Resin^+)_2\text{-}M(CN)_4^{2-} + 2H_2SO_4 \longrightarrow (Resin^+)_2SO_4^{2-} + MSO_4 + HCN$$

The eluate, containing metal sulphates and HCN was passed downflow through a cation exchange column for recovery of the metals.

$$2\ Resin^-H^+ + MSO_4 \longrightarrow (Resin^-)_2M^{2+} + H_2SO_4$$

The effluent from the cation exchange column, containing HCN and sulphuric acid, was collected in a 1.4 N NaOH trap. Any gaseous HCN not collected in the primary trap was recovered in a secondary caustic aspirator trap. The metals (Cu, Zn, Ni) were recovered by brine desorption of the cationic exchange resin.

The loading capacities for cyanide and the base metals on the resin apparently were calculated from the amount of each recovered in the caustic traps and brine eluate, respectively, during elution. There was no mass balance for the amount of cyanide and base metals removed from the mill effluent during adsorption on the anionic and cationic exchange resins, and the amounts eventually recovered during the elution process.

The overall percent recovery of cyanide is of the utmost importance since the ability to recycle the cyanide back to the cyanidation leach circuit plays a major role in the economic viability of the whole ion exchange process.

Furthermore, in a full scale operation, the cyanide most likely would be recovered from the acidic regenerant solution in a scrubber column, where the acidic solution would pass downflow countercurrent to a stream of air. The air would displace the HCN from the regenerant solution. The air and HCN would then pass upflow through an absorber column where it would be contacted countercurrently with an alkaline absorber solution. The HCN would be removed through the air stream and trapped as CN^-. Since the cyanide would be released from the regenerant solution as HCN, the overall percent recovery is important due to safety considerations as well as economic considerations.

The overall percent recovery of the base metals would indicate which metals, if any, were not fully removed from the resin during elution, and therefore might be acting as resin poisoning agents. This information was not obtained during the original CANMET report by Gilmore (12).

During the present work, the overall percent recovery of cyanide was investigated stepwise. First of all, the amount of cyanide present in an acidic regenerant solution, which can be released as HCN and then recovered in an alkaline trap, was determined. The results of this testwork are reported in Appendix III Section 2.2, "Recovery of HCN from Acidic Regenerant Solution".

Secondly, the elution procedure for removal of base metals and cyanide from loaded anionic exchange resins was investigated. In addition to the 1% sulphuric acid eluant which CANMET utilized, a second stripping procedure which was developed by Witteck in conjuncton with Lac Minerals in 1981, was tested. The removal of cyanide and base metals from the resin was quantified, and the concentration of reagents in the regenerant solution optimized. The results of this work are reported in Appendix III Section 2.3 "Elution of Resin Loaded with Metal Cyanide Complexes".

Elution isotherms were generated and are reported in Appendix III, Section 2.4.

Twenty-two adsorption/elution cycles were carried out on column I, and a mass balance was maintained for Cu, Fe, Ni and Zn. The overall loss in resin capacity after 22 cycles was determined. The results of this testwork are presented in Appendix III, Section 2.5.

Potential resin poisoning agents were investigated, using "spiked" mill effluent (Sb, As, Co, Hg and Mo). These results are provided in Appendix III, Section 2.6, along with the results of testwork on selective elution procedures for their removal from the "poisoned" resin.

Finally, testwork was performed on an effluent from the Hemlo area in an attempt to identify a resin and the conditions required to remove antimony and arsenic from waste effluent using ion exchange resins. The results of this work are provided in Appendix III Section 2.7.

A summary of the results is provided below.

5.2.2 Recovery of HCN from an Acidic Regenerant Solution

In order to evaluate the trapping of HCN using an alkaline trap, a series of six tests was carried out. For the initial five tests, a synthetic solution, containing sulphuric acid (pH 0.7 to 1.5) and sodium cyanide, was used to mimic the acidic regenerant solution during elution. In two of these tests (Test 1 and 2) base metals (Cu and Zn) were added to mimic more closely the regenerant solution for the primary column, and to determine if the presence of base metals has any inhibitory effect on the release of HCN from acidic solution. For the sixth test, resin loaded with metal cyanide complexes was eluted, and the HCN recovered. A number of different solutions were tested for the alkaline trap, including sodium hydroxide, as well as mill effluent, pH adjusted with either sodium hydroxide or lime. The detailed procedures and experimental results for the six tests are provided in Appendix III Section 2.2. A summary of the results is provided in Table 9.

Table 9

SUMMARY OF TESTWORK ON THE RECOVERY OF HCN IN ALKALINE ABSORBERS

Test	Cyanide Present g	Metals Present	Absorber Solution	Cyanide* recovered in Traps %	Time Required hours
1	17.1	Yes	NaOH	11	46
2	17.1	Yes	Effluent & NaOH	94	42
3	9.96	No	Effluent & Lime	75	na
4	4.98	No	Effluent & Lime	90	6
5	4.99	No	Effluent & Lime	85	6
6	1.20	Yes	Effluent & Lime	92	6

* Includes cyanide present in samples

The results of the testwork indicated the following:

- the alkaline absorber solution must be maintained at pH 12 in order to reduce the leakage of HCN from the trap to less than 1% of the total cyanide present (pH was not maintained during test 1).

- mill effluent maintained at pH 12 using NaOH or lime could be used as the absorber solution. For the two column technology, a portion of the column I effluent, which contains only lime, free cyanide and thiocyanate, would be appropriate after pH adjustment.

0656A

WD1

- if lime is used to maintain the pH, a second absorber trap may be required to trap HCN lost from the primary trap.

- if mill effluent is used, (or water pH adjusted using lime) solids ($CaCO_3$) will form in the absorber column due to the absorption of CO_2 into the alkaline solution.

- at least on a laboratory scale, sparging air through the regenerant and absorber tanks is more effective for scrubbing and absorbing HCN than are the use of conventional countercurrent scrubber/absorber columns.

- greater than 90% of the cyanide present in an acidic regenerant solution can be recovered in an alkaline absorber solution within 6 hours.

- stripping of resin loaded with metal cyanide complexes also results in the trapping of 92% of the cyanide originally on the resin into the absorber solution within 6 hours.

- the presence of base metals in the acidic regenerant did not affect the time required to remove the HCN from the solution.

- a mill effluent trap can be enriched from 0.5 g/L to at least 10 g/L CN.

5.2.3 Elution of Resin Loaded with Metal Cyanide Complexes

Prior to carrying out adsorption/elution cyclic testwork, six elution tests were carried out on resin loaded with metal cyanide complexes, in order to optimize the elution procedure and to ensure high percent recoveries of base metals and cyanide from the resin.

The regenerant solution used by CANMET for column I was a 1% sulphuric acid (0.1 M) solution. Prior work at Witteck had shown that acid alone does not remove copper efficiently. Witteck Development Inc., in collaboration with Lac Minerals Inc., carried out testwork in 1981 to optimize the removal of copper from resins loaded with metal cyanide complexes. The testwork led to the filing of a joint provisional patent which covered the use of a new regenerant solution, which consisted of an acidic solution containing a second reagent which will be referred to as the WDI/Lac reagent. In the initial testwork on the elution of loaded resins, the CANMET and Witteck/Lac processes were compared for the removal of base metals and cyanide from the resins.

The resin used for this testwork was Lewatit MP-500, which had been loaded previously using effluent A. The resin was eluted in a column according to the procedures described in detail in Appendix III Section 2.7.

The results indicated that the WDI/Lac regenerant solution eluted copper much better than a 1% sulphuric acid solution. Under similar conditions, the 1% sulphuric acid solution eluted only 16% of the copper compared to greater than 99% using the process developed previously at Witteck.

Nickel was eluted effectively (92%) by the WDI/Lac eluant. Greater than 99% of the zinc was removed from the resin using either eluant.

Iron acted as a poisoning agent with either eluant. Section 5.2.6 provides more information on the removal of iron cyanide complexes from strong base anoinic exchange resins.

More than 99% of the cyanide present on the resin was removed during elution using the WDI/Lac eluant.

5.2.4 Elution Isotherms

Elution isotherms were produced in order to compare the CANMET elution process using 1% sulphuric acid to the WDI/Lac elution process. The percent recovery of base metals and HCN in the acidic regenerant solution were compared, as well as the required volume of eluant. Elution isotherms were produced, and are provided in Appendix III Section 2.4, along with a detailed description of the experimental procedures and results. A summary of the results is provided in Table 10 below.

Table 10

COMPARISON OF CANMET AND WITTECK/LAC ELUANTS FOR RECOVERY OF CYANIDE AND BASE METALS FROM RESIN

Sample	Amount, g (% Removal)					
	CN(t)		Cu		Zn	
Loaded Resin (50 mL)	3.12		1.87		1.79	
Column I - CANMET Strip	3.06	(98%)	0.13	(7%)	1.53	(85%)
Column II - WDI/Lac Strip	2.88	(92%)	1.78	(95%)	1.79	(100%)

0656A

The CANMET eluant desorbed the loaded resin after sixty bed volumes of 0.1 M H_2SO_4. At this point the eluate contained 0.033 g/L CN(t). Ninety-eight percent of the total cyanide, and eighty-five percent of the zinc was removed from the resin using this procedure. However, ninety-three percent of the copper remained on the resin bed.

The WDI/Lac eluant desorbed the same resin after sixty bed volumes. A sample of the final eluate contained only 0.001 g/L CN(t). This process removed 92% of the cyanide, 100% of the zinc as well as 95% of the copper.

It is concluded that the WDI/Lac regenerant represents an improvement over the original elution technique proposed by CANMET when high levels of copper are present in the mill effluent.

5.2.5 Cyclic Adsorption/Elution Testwork

Cyclic testwork was carried out on column I of the two column process in order to observe any decrease in capacity due to the build up of resin poisoning agents. Resin (Lewatit MP-500) was loaded and eluted 21 times. A mass balance was obtained for copper, iron, nickel and zinc throughout the 21 cycles.

The feed solution (effluent A) contained the following species (mg/L): CN(t), 500; SCN, 150; Cu, 214; Fe, 0.06-3.4; Ni, 5.4; and Zn, 140. Antimony, arsenic, cobalt, lead and molybdenum were below the detection limit (< 0.1 mg/L) in the feed effluent.

The resin was eluted using the WDI/Lac procedure. Elution was carried out for 7 hours per cycle.

The experimental procedure and results are provided in detail in Appendix III Section 2.5.

0656A

The results are summarized below for each species present in the feed effluent.

Copper

No significant build up of copper on the resin occurred over the 21 cycles. Optimization of the WDI/Lac elution process indicated that 0.1 M acid with WDI/Lac reagent was sufficient for elution of copper.

For three cycles, base metals were allowed to accumulate in the regenerant soluton, i.e. spent regenerant was replenished with acid and WDI/Lac reagent and reused for subsequent cycles. A decrease in stripping efficiency was noted during these three cycles. When the copper concentration in the regenerant increased from 0.4 g/L to 0.7 g/L the copper recovery decreased from 99% to 73%, respectively. When fresh regenerant was used, the elution efficiency was restored. After 21 cycles, 88% of the copper which had loaded onto the resin had been recovered during elution.

Zinc

After 21 cycles of adsorption/elution, 100% of the zinc loaded on the resin had been recovered. However, as with copper, when spent regenerant was replenished and reused, the zinc recovery during elution decreased to only 12% recovery. When fresh regenerant was used subsequently, the resin was fully desorbed with respect to zinc.

Nickel

No significant build up of nickel on the resin was observed during the 21 cycles of adsorption/elution testwork. After 21 cycles, 98% of the nickel which had loaded on the resin had been recovered during elution.

0656A

Iron

Iron was clearly identified as a resin poisoning agent during the cyclic testwork. After 20 cycles, 92% of the iron remained on the resin.

In subsequent sections (Section 2.6), methods of eluting iron from strong base anionic exchange resin were tested, and the results are summarized.

Cyanide

Since the primary function of column I is the removal of metal cyanide complexes from waste effluent streams, no attempt was made to quantify the recovery of cyanide throughout the full 21 cycles. The amount of cyanide not removed from the resin during each elution cycle can be estimated from the metals analyses and recovery data. Only iron acted as a poisoning agent, and iron was present in the feed solution at very low concentration.

However, for cycle 1, cyanide adsorption and elution data was obtained. Ninety-four percent of the cyanide loaded on the resin was recovered in the alkaline trap after 7 hours of elution using the WDI/Lac procedure. This percent cyanide recovery is in agreement with the elution data provided in the previous sections (Sections 5.2.2, 5.2.3 and 5.2.4).

For eight of the cycles, the same alkaline solution remained in the absorber trap, and the cyanide concentrations were allowed to build up. The concentration of cyanide in the alkaline absorber solution reached 6000 mg/L without any loss in absorption efficiency. After eight cycles, the second trap, containing pH 12 sodium hydroxide solution, contained less than 1% of the cyanide.

0656A

In a plant situation, the cyanide concentration in the alkaline trap would be built up to the point where the alkaline solution was no longer trapping 99% of cyanide. Alternatively, two traps could be used in sequence, and the cyanide concentration of the first could be increased to either the point of saturation, or to the point where the second trap began to loose its efficiency, whichever came first. At this point, the solution in the first trap would be recycled to the leach circuit, trap 2 would become trap 1, and a fresh alkaline solution would be added as trap 2.

As already mentioned above, a portion of the column effluent from column I, containing only free cyanide and lime, could be used rather than fresh water and NaOH. In this case, however, the formation of $CaCO_3$ would require attention.

Overall Loss in Loading Capacity

After 20 cycles, the apparent loading capacity had reduced to only 52% of the initial capacity observed during cycle 2. In contrast, however, the assay data implied that only iron had poisoned the resin, and only to the extent of 2.7 mg Fe/g resin. Not enough poisoning had occurred to account for the observed loss in loading capacity.

Since the effluent A did not contain detectable levels of Sb, As, Co, Pb or Hg, only thiocyanate could account for the observed loss in capacity. However, work reported elsewhere (see Section 5.4) indicated that although thiocyanate does load on to the primary column, it is also eluted efficiently during the stripping cycles.

An elution procedure published by Mintek (18) described a method of stripping aurocyanide and most base metal cyanide complexes including iron cyanide from strong base resins using NH_4SCN.

The thiocyanate, in turn, is removed from the resin using Fe(III). Witteck tested this procedure in two different ways to investigate the observed loss in loading capacity.

Firstly, a solution of Fe(III) was passed through the resin bed after cycle 20 according to the second part of the Mintek procedure (18). The eluate was assayed for thiocyanate to determine if thiocyanate had accumulated on the resin. The resin was then reloaded during cycle 21 to determine if full loading capacity had been restored.

Very little thiocyanate (0.0006 M) was obtained in the Fe(III) eluate, and the observed loading capacity during cycle 21 remained at only 56% of the initial capacity after this procedure. This confirmed that thiocyanate had not accumulated on the resin during the first 19 cycles.

Secondly, after stripping during cycle 21, a solution of NH_4SCN was passed through the resin bed to remove any metals remaining on the resin bed. This was followed by a solution of Fe(III), according to the full Mintek procedure. Following the Mintek strip, the resin was reloaded, and the observed capacity was only 71% of the original capacity. While 15% of the lost capacity was restored using the full Mintek procedure, 30% of the capacity was still lost.

To determine if the apparent loss in resin capacity was real, fresh resin was loaded concurrently with the reloading of the cyclic resin after the Mintek strip (cycle 22). Fresh resin loaded to 28 mg of metals/mL of resin compared to 34 mg of metals/mL of resin for the cyclic resin.

Therefore, it was concluded that the apparent 30% loss in resin capacity was not due to poisoning of the resin, but was due to a change in the composition of the feed effluent, other than the concentrations of the base metals followed during this study.

An increase in the total ionic strength of the feed effluent, would for example, affect the equilibrium established between the ions on the resin and the ions in solution during adsorption.

As a final confirmation that there was no significant amount of metals remaining on the resin, the final, eluted resin was assayed and was found to contain 0.4% Fe, 0.1% Pb, 0.2% CN(t), 0.02% Co and less than 0.01% Cu, Hg, Mo, Ni and Zn.

Therefore, it is concluded that a periodic elution step utilizing the Mintek procedure would be useful for the removal of resin poisoning agents. However, variation in the loading capacity of the resin can be expected with fluctuations in the feed composition.

5.2.6 Resin Poisoning Agents

Effluent A, which was used for the cyclic testwork, did not contain detectable levels of antimony, arsenic, cobalt, mercury or molybdenum. Therefore, it was not known if anionic exchange resins would remove these metals efficiently from cyanide waste effluent, and if so, if they could be recovered from the resin using the same elution process as was used for the base metals.

5.2.6.1 Adsorption/Elution Cyclic Testwork using Enriched Cyanide Waste Effluent

Since none of the effluent solutions received by Witteck at this stage in the testwork contained high levels of all of the above metals, effluent A was spiked with each of Sb, As, Co, Hg and Mo, and further cyclic testwork (8 cycles) was carried out as described above in Section 5.2.5. for the as-received effluent A.

The experimental procedures and detailed results are provided in Appendix III, Section 2.6.

Table 11 summarizes the effectiveness of Lewatit MP-500 in the sulphate form for removal of antimony, arsenic, cobalt, mercury and molybdenum from the enriched effluent A.

Table 11

RECOVERY OF Sb, As, Co, Hg AND Mo USING A STRONG BASE RESIN

Metal	Sb	As	Co	Hg	Mo
Efficiency:					
Loading	No	No	Yes	Yes	No
Elution	No	--	No	No	No

Cobalt and mercury were removed from the mill effluent by the resin, producing barren levels in a 40 bed volume composite sample of only 0.4 mg Co/L and 0.02 mg Hg/L, and loading to 9.6 and 8.6 mg metal/g resin, respectively, after eight cycles (200 bed volumes). The other three metals were not removed efficiently from the waste effluent, leaking greater than 1 mg/L of the metal in the 40 bed volume composite sample of column effluent.

Table 11 also includes a summary of the elution results. The elution process which was found to be effective for the recovery of copper, nickel and zinc from the resin, was not effective at removing antimony, cobalt, mercury nor molybdenum from the resin. The two most common resin poisoning agents, iron and cobalt, were studied in further elution testwork below (see Section 5.2.6.2). Further testwork on the loading and elution of antimony and arsenic is discussed in Section 5.2.7 and 5.4.

5.2.6.2 Removal of Iron Cyanide from Strong Base Resin

In order to determine the best method for the elution of iron cyanide from strong base anionic exchange resins, a series of six elution tests were carried out testing six different eluants. For this testwork, resin (MP-500) was batch loaded with a solution containing a 50:50 mixture of potassium ferrocyanide and potassium ferricyanide.

The amount of iron on the resin was determined prior to and at completion of each elution test.

The detailed experimental procedures and results are provided in Appendix III Section 2.6.2. The six eluants tested, and a summary of the results is provided in the following table.

Table 12

ELUTION TESTWORK ON THE REMOVAL OF IRON CYANIDE COMPLEXES FROM STRONG BASE RESINS

Test	Eluant	Iron on Resin mg	Iron Recovered in Eluate		
			First 50 mL	Second 50 mL	Total Percent
1	1 M NH_4SCN 0.5 M NaOH	4.76	4.1	0.73	101
2	1 M NH_4Cl 0.5 M NaOH	4.75	0.04	0.12	3.4
3	1 M $(NH_4)_2SO_4$ 0.5 M NaOH	4.59	0.028	0.023	1.1
4	1 M $NaHCO_3$ 0.5 M NaOH	4.54	0.018	0.025	0.95
5	1 M $NH_4O_2C_2H$ 0.5 M NaOH	4.50	0.006	0.006	0.26
6	1 M Citric Acid 1 M NaOH	4.49	0.022	0.023	1.0

0656A

The Mintek (18) eluant (test 1) was far superior to the other eluants tested. One hundred percent of the iron was removed from the resin in 10 bed volumes of eluate.

For waste effluent solution containing low levels of iron cyanides, the resin bed could be eluted periodically using this method. The eluate, containing iron thiocyanates, can be treated with any alkali or base. The iron will precipitate from the solution as ferric hydroxide and may be filtered, redissolved in sulphuric or nitric acid and recycled to the regeneration stage.

The filtrate, containing thiocyanate may be recycled to the elution step. In this manner, Mintek (18) has shown this procedure to be efficient and economical; the overall consumption of thiocyanate and ferric ions is theoretically zero.

5.2.6.3 Removal of Cobalt Cyanide from Strong Base Resins

The Mintek strip for the elution of base metal cyanide complexes from strong base resins was tested for the elution of $Co(CN)_6^{3-}$ from Lewatit MP-500.

The detailed procedures and results are provided in Appendix III, Section 2.6.3. Resin was loaded with a synthetic solution of $Co(CN)_6^{3-}$, and then eluted by the procedure described in the recent Mintek report (18), using NH_4SCN.

The elution was successful. After 12 bed volumes of eluant had passed through the resin bed, 93% of the cobalt had been recovered; 100% was recovered within 20 bed volumes.

While the Mintek process is recommended for the periodic removal of cobalt and iron, the WDI/Lac process is recommended for the routine elution of the more common base metals which occupy the bulk of the resin capacity. The WDI/Lac process utilizes inexpensive reagents and is a one-step process. Elution returns the resin to the active form; no separate regeneration stage is required.

5.2.7 Removal of Antimony and Arsenic from Mill Effluent Using Ion Exchange Resins

In total, thirty-three tests were carried out in an attempt to find conditions under which an ion exchange resin might remove antimony and arsenic efficiently from mill effluent solutions. Both macroporous and gel anionic exchange resins in a variety of forms (SO_4 Cl, OH) were tested, as well as one cationic exchange resin. Attempts were made to alter the speciation of the complexes by altering the pH and redox potential of the mill effluent prior to contact with the resin. In addition, the use of a scavenger column was investigated for the removal of antimony and arsenic from mill effluent that had been passed through column I for the removal of base metal cyanide complexes.

In all cases, the loading efficiencies were poor. For the feed effluent tested (25 to 40 mg/L Sb), antimony loaded to about 0.14 mg/mL resin when contacted batchwise with 5 bed volumes of effluent, and to 1 mg/mL resin when contacted batchwise with 50 bed volumes of effluent. Under these conditions, breakthrough would occur within 3 bed volumes.

Further testwork is required to determine the best method for the removal of antimony and arsenic from gold mill effluent in conjunction with the ion exchange process for removal and recovery of base metals and cyanide.

0656A

5.3 COLUMN II TESTWORK

The first column of the two column system was designed to remove the metal cyanide complexes from cyanide waste solution. The second column, consisting of a strong base resin in the sulphate form preconditioned with cuprocyanide, was tested for the removal of free cyanide from the resulting effluent. This section summarizes the work carried out on Column II.

5.3.1 Background

In the 1976 CANMET report by A.J. Gilmore (12), the adsorption cycle for column II typically displayed "royal barren" behaviour during the initial bed volumes of column effluent. This "royal barren" effluent was caused by the leakage of cyanide, and in most cases copper from the resin bed during adsorption. It was concluded that unadsorbed free cyanide was dissolving the copper cyanide on the secondary column. Although the "royal barren" effluent could be recycled, this was not deemed to be an viable operation. Instead, the 1976 report tested and recommended the operation of two sulphate columns in series and concluded that this operation was more efficient at achieving column effluent containing less than 0.1 ppm CN(t) than the operation of the cuprocyanide form of the resin as the secondary column.

Witteck undertook to reinvestigate the efficiency (loading capacity, barren levels) of the cuprocyanide resin for the production of effluent containing less than 0.1 ppm CN(t), and to compare it to other forms of a strong base resin.

The reinvestigation centred on three aspects of the operation: the preconditioning stage, the bleeding of cyanide and copper during adsorption, and the removal of copper during adsorption and elution. The results of this testwork are summarized in Sections 5.3.2 and 5.3.3. The results of the testwork on other forms of anionic exchange resins are summarized in Section 5.3.4. The experimental procedures and detailed results of the testwork are provided in Appendix III, Section 3.0.

5.3.2 Preconditioning Step

In the 1976 CANMET report (12), Goldblatt's (2) method of preconditioning the column was used. Goldblatt stated that once the resin was loaded with copper cyanide, it was washed with water and eluted with 1% sulphuric acid until the cyanide concentration in the eluate dropped to less than 1000 mg/L NaCN. The column, after water washing, was ready for adsorption of free cyanide. There was no indication of the concentration of cyanide in the column effluent during or following the water wash. It was suspected that elution with dilute acid to less than 1000 mg/L NaCN in the eluate was insufficient, as a free cyanide concentration below 0.1 mg/L was desired in the column effluent during the loading cycle. Witteck decided to investigate if prolonged elution with dilute acid followed by water would produce an eluate with significantly lower cyanide concentrations, and if so, if this would reduce or eliminate the leakage of copper and cyanide from the column during the initial bed volumes of the loading cycle, thereby reducing or eliminating the royal barren behaviour.

In summary, the results indicated that prolonged washing with 1% sulphuric acid would reduce the leakage of cyanide from the resin during adsorption (from 0.25 mg/L to 0.18 mg/L cyanide), but not to below the 0.1 mg/L target value. It was concluded that while prolonged washing with 1% sulphuric acid followed by water is important, it will not eliminate the royal barren behaviour.

5.3.3 Cyclic Testwork

In the 1976 CANMET report (12), Gilmore carried out one adsorption/elution cycle for each of six mill effluents. During the initial adsorption cycle, royal barren behaviour was observed. Since careful cleaning of the preconditioned resin (Section 5.3.2) did not eliminate this occurrence, cyclic adsorption/elution testwork was carried out to determine if the leakage of cyanide and copper from the cuprocyanide resin might decrease with subsequent cycles, i.e. if royal barren behaviour was a first cycle phenomena.

Six adsorption/elution cycles were carried out during the test program. In addition to following the cyanide and copper levels in the column effluent during adsorption, the leakage of copper from the column during elution was monitored in order to quantify the amount of copper removed from the resin during each cycle. This would be expected to affect both the loading capacity for free cyanide and the required frequency of reconditioning the resin.

The details of the experimental procedures and results are provided in Appendix III, Section 3.3. In summary, six cycles of adsorption and stripping were carried out on the column II technology using Amberlite IRA-400 resin in the sulphate form preconditioned with cuprocyanide. Throughout these cycles a mass balance was maintained for copper on the resin, as well as for cyanide removed from the effluent during adsorption and recovered during elution.

In order to observe any net loss in equilibrium capacity after six cycles due to the loss of copper from the resin, care was taken during the first and final cycles to ensure that full equilibrium capacity was attained during loading.

A summary of the percent cyanide recovered during each cycle, and the amount of copper removed from the preconditioned resin during each stage is provided in Table 13.

5.3.3.1 Cyanide Recovery

The percent cyanide recovered for each cycle varied from 90 to 99.9%. The overall recovery of cyanide after six adsorption and elution cycles was greater than 95%.

5.3.3.2 Equilibrium Capacity - Loss of Copper from Resin

After six adsorption/elution cycles, the equilibrium loading capacity (29.2 mg CN/mL resin) was 93% of that observed during the first loading cycle using fresh preconditioned resin (31.5 mg CN/mL resin). This 7% loss in loading capacity occurred concurrently with a 19% loss of copper from the preconditioned resin. The loss in capacity is explained (see Appendix III, Section 3.3) by the reduced capacity of the sulphate form of the resin with respect to the cuprocyanide form. Loss of cuprocyanide from the resin converts those sites on the resin to the sulphate form after elution with sulphuric acid.

0656A

WD1

Table 13

CYCLIC TESTWORK: COLUMN II

Stage	Time Min.	Cyanide Loaded mg	Cyanide Recovered mg	Cyanide Recovered %	Copper Removed mg	Copper Remaining mg
Precondition	-	-	-	-	-	1017
Load 1	360	1575	-	-	8	1009
Strip 1	430	-	1540	97.8	53	956
Load 2	260	1398	-	-	2	954
Strip 2	407	-	1396	99.9	22	932
Load 3	270	1418	-	-	7	925
Strip 3	420	-	1411	99.5	70	855
Load 4	270	1353	-	-	19	836
Strip 4	380	-	1266	90.5	2	834
Load 5	265	1259	-	-	5	829
Strip 5	540	-	1189	94.4	2	827
Load 6	317	1458	-	-	5	822
Strip 6	460	-	1331	91.3	1	821
Overall		8463	8093	95.6	196	821

0656A

Although copper leaked from the column during every loading cycle, the amount removed during elution decreased with subsequent cycles. Further research involving more cycles would be required to determine how frequently the cuprocyanide form of the resin would require a reconditioning process.

5.3.3.3. Loading Isotherms: Royal Barren Behaviour and Breakthrough Capacity

Behaviour similar to the "royal barren" behaviour described by Gilmore was observed during the present work. For three of the six cycles (cycles 1, 5 and 6), periodic samples of the column effluent were assayed for cyanide and copper to produce loading isotherms (Figures are provided in Appendix III Section 3.3). In all cases, the cyanide concentrations in the column effluent exceeded the 0.1 mg/L CN(t) target during the first 10 bed volumes. The cyanide levels then decreased, (in cycle 6 the 0.1 mg/L CN(t) target was attained briefly), prior to breakthrough.

It was hoped that the royal barren behaviour observed by Gilmore was a first cycle phenomena and that it would disappear with subsequent cycles. Unfortunately, this was not the case.

It is concluded that the cuprocyanide form of the resin would not be adequate for provinces where government guidelines specify a limit of 0.1 ppm CN(t) in discharge waters. However, it would provide adequate capacity for areas where the government specification was less than 1 ppm CN(t). The observed breakthrough capacity [breakthrough at 1 ppm CN(t)] for this resin was 16 to 20 mg CN(t)/mL resin.

The loading isotherms for copper (see Appendix III) mimicked the cyanide curves prior to cyanide breakthrough, reaching levels in excess of 1 ppm Cu in the column effluent. After cyanide breakthrough, the copper levels decreased rapidly to below 0.1 ppm Cu. It is concluded that the government guidelines for copper would be exceeded in the column effluent prior to cyanide breakthrough, and that leakage of copper during loading would prohibit by itself the discharge of the column effluent to the environment.

5.3.4 Other Forms of Amerlite IRA 400

The present testwork confirmed Gilmore's observations concerning the use of the cuprocyanide form of the resin for removal of free cyanide from gold mill effluent. Since this form of the resin will not meet consistently a target level of 0.1 ppm CN(t) in the column effluent, other forms of a strong base resin were investigated for comparison. Gilmore had tested and recommended resin in the sulphate form for the secondary column. This form of the resin was included in the present testwork, as was the hydroxide form of Amerlite IRA-400. The latter was chosen since, of all the simple anions, hydroxide ion typically has the lowest affinity for strong base anionic exchange resins. Therefore, hydroxide ion was expected to exchange more readily with free cyanide.

The hydroxide and cuprocyanide forms of the resin displayed sharper loading isotherms than did the sulphate resin, at the same flow velocity. A comparison of the three forms of the resin is provided in the summary table below. More detail is provided in Appendix III, Section 3.4.

Table 14

COMPARISON OF CUPROCYANIDE, SULPHATE AND HYDROXIDE FORMS OF IRA-400

Capacity Level	Bed Volumes			Capacity, mg CN/mL Resin		
	CuCN	SO_4	OH	CuCN	SO_4	OH
Breakthrough						
(a) 0.1 ppm (CN(t)	0	10	30	0	5.1	15.3
(b) 1 ppm CN(t)	40	15	30	20.4	7.6	15.3
Equilibrium	90	> 140	70	31.9	n.d.	25.1

The sulphate form of the resin is the poorest at removing cyanide from solution. Although it does produce barren effluent containing less than 0.1 ppm CN(t) for the first 10 bed volumes, the capacity to breakthrough at 0.1 ppm CN(t) is only 5 mg CN/mL resin. Capacity to breakthrough at 1 ppm CN(t) is only 7.6 mg CN/mL resin.

The cuprocyanide form has the highest capacity at breakthrough, 20 mg CN/mL resin. However, for this resin breakthrough must be defined as 1 ppm CN(t); this resin does not meet the target level of less than 0.1 ppm CN(t). An equilibrium loading capacity of 32 mg CN/mL of resin was attained after 90 bed volumes.

The hydroxide form of the resin was superior on most accounts. It removed cyanide from the effluent to below 0.1 ppm CN(t), loading to a capacity of 15 mg CN/mL resin at breakthrough [0.1 or 1 ppm CN(t), breakthrough was very sharp] and to a capacity of 25 mg CN/mL resin at equilibrium. Although the equilibrium capacity was lower than that observed for the cuprocyanide form, optimization of the flow velocity during loading could improve the observed capacity.

0656A

It is concluded that for areas where government guidelines specify cyanide levels of less than 0.1 ppm CN(t) in discharge waters, the hydroxide form of the resin would be the best form tested to date. However, if levels 1 ppm CN(t) are allowed, the cuprocyanide form of the resin may display higher breakthrough and equilibrium loading capacities. The sulphate form of the resin is not recommended for further work.

5.4 Column I and Column II Operated in Series

In the last part of the testwork, column I and column II were coupled and operated in series. Column I contained 50 mL of Amberlite IRA-400 in the sulphate form. Column II contained 50 mL of Amberlite IRA-400 in the sulphate form preconditioned with cuprocyanide, as described in Appendix III. All species present in the cyanide waste effluent solution were followed during this testwork. The feed solution was mill barren, effluent B, and contained levels of antimony, arsenic, cobalt, lead and molybdenum.

The experimental procedures and detailed results are provided in Appendix III; a summary of the results is provided in Table 15. The deportment of each species is discussed below.

5.4.1 Deportment of Co, Cu, Fe, Pb, Mo, Ni and Zn

The base metals Co, Cu, Fe, Pb, Mo, Ni and Zn are removed from the mill effluent by the primary column. Molybdenum, however, showed early breakthrough from column I during the second cycle of this testwork, indicating a lower affinity for the resin than the other base metals.

Nickel and zinc were eluted efficiently from column I using the WDI/Lac reagent in dilute acid. Twenty percent of the cobalt and sixty percent of the iron remained on the resin after elution, poisoning the resin. Insufficient quantities of lead and molybdenum were loaded on to the resin during the adsorption cycle to accurately determine how efficiently they were recovered during the elution cycles. More testwork, using a feed solution containing higher concentrations of Mo and Pb, would be required to accurately follow these two metals.

Table 15

DEPORTMENT OF ALL METALS, CYANIDE AND THIOCYANATE DURING TWO COLUMN CYCLIC TESTWORK

Species	Feed mg/L	Loads on to Column I	Loads on to Column II	Barren Levels mg/L	Percent Recovered during Elution Col.I	Col.II
Sb	1.34	Partial	No	High	100	-
As	8.72	No	Partial	High	100	98
Co	2.04	Yes	-	0.05	79	-
Cu	64	Yes	-	0.01	69	-
Fe	14.6	Yes	-	0.02	40	-
Pb	0.14	Yes	-	0.05	-	-
Mo	0.23	Yes	-	0.01	-	-
Ni	56	Yes	-	0.1	99	-
Zn	59	Yes	-	0.05	99	-
SCN	240	Yes	Yes	1	100	100
CN(t)	617	Yes	Yes*	0.2	86	80

* Free cyanide

0656A

Recovery of copper during elution of column I was poor. This low copper recovery (79%) is in disagreement with the results observed and reported in Section 5.2 for the column I elution testwork. The only variable with respect to the elution and cyclic testwork reported in Section 5.2 was that Amberlite IRA-400, rather than Lewatit MP-500 was used during this phase of the work. It may be that cuprocyanide is not removed as efficiently from the Amberlite IRA-400 resin using the WDI/Lac reagent as it is from the Lewatit MP-500 resin.

5.4.2 Deportment of Sb and As

Arsenic partially loaded on to both the primary and secondary columns, but was readily displaced by other species which have a higher affinity for the resin. Antimony loaded to low capacity on the first column, but did not load to any extent on the second column. Both of these metals were present in the column II effluent. Breakthrough of both elements occurred in the initial bed volumes, and quickly reached the levels in the feed solution. Resin analyses indicated that the amount that loaded was eluted readily from both columns during the elution cycles.

5.4.3 Deportment of SCN

Thiocyanate loads on to the primary column. Breakthrough occurs in advance of cyanide breakthrough. Thiocyanate in the column I effluent is removed from solution by the secondary column. Resin analyses indicated that thiocyanate was eluted efficiently from both columns during the stripping cycles.

5.4.4 Deportment of CN(t)

In total, column I loaded 2425 mg CN(t) and column II loaded the remaining 845 mg CN. The column II effluent contained less than 0.2 mg/L cyanide during the first cycle. During the second cycle, cyanide leaked from the second column during the first 30 bed volumes. Once again, the use of this form of the resin to achieve effluent consisting of less than 0.1 mg/L cyanide is unlikely.

Elution removed 76% of the cyanide from column I, and 82% of the cyanide from column II, according to the resin analyses. This is in fair agreement with the analyses of the alkaline traps, which recovered in total 86% and 80% of the cyanide from column I and II, respectively, after two cycles.

6.0 CONCLUSIONS AND RECOMMENDATIONS

As a result of completing the prescribed work for DSS Contract 03SQ.23440-5-9121, the following conclusions and recommendations are made.

1. The literature search revealed that since the original CANMET work carried out in the 1970's, only limited research has been conducted on the use of resins for the removal of cyanide from gold mill effluent solutions. The technology developed by CANMET had not been further investigated, and no major improvements to the general technology were documented.

2. The industry survey produced responses which demonstrated that the current level of environmental concern about cyanide may not be as warranted as was assumed at commencement of this contract. As a result of natural degradation, many operations are coming very close to meeting government specifications. Guidelines vary from province to province, and indeed some operations are dealt with on an individual site-specific basis. Thus, many operations stated that they do not have a problem with effluent treatment for cyanide. Furthermore, most of the effluent treatment technologies available to date have the ability to produce an environmentally acceptable effluent.

   Therefore, it was quite clear that implementation of an ion exchange process for effluent treatment would be considered only on an economic basis. If the ion exchange process could recover cyanide for recycle to the mill, it would be very attractive economically due to the operational cost savings. To this end, it is imperative

that the both the metal complexed cyanide and the "free" or uncomplexed cyanide be recovered by the treatment process.

3. The results of the bench scale testwork carried out on the CANMET two column technology indicated acceptable base metal content of barren effluent but leakage of cyanide from the second column caused the target level of 0.1 ppm total cyanide to be exceeded. A new form of the resin was tested (hydroxide form) and it did achieve the target, but the equilibrium cyanide loading was slightly lower. The choice of resin for column II deserves further investigation. Overall, this technology can recover greater than 90% of the cyanide from waste streams into a concentrated sodium cyanide solution for recycle.

   In contrast, neither arsenic nor antimony were removed efficiently from solution using the two column ion exchange technology. It is recommended that any further testwork utilizing ion exchange address the problem of removal and disposal of these two toxic metals.

   Elution testwork indicated that while the eluant recommended by Gilmore removed most base metals efficiently from the loaded resin, the CANMET procedure did not fully recovery copper cyanide. After comparison, the stripping procedure developed in 1981 by Witteck Development Inc. in collaboration with Lac Minerals Ltd., is recommended for use in any further testwork on column I elution. The eluant recommended by CANMET for elution of column II was found to be sufficient.

7.0 REFERENCES

1. Burstall, F.H. et al. Ion exchange process for the recovery of gold from cyanide solution. Ind. Eng. Chem., vol. 45, 1953. P.1648.

2. Goldblatt, E. Recovery of cyanide from waste cyanide solutions by ion exchange. Ind. Eng. Chem., vol. 51, 1959. p. 241.

3. Gilmore, A.J. and Gow, W.A. Cyanide recovery from gold-barren waste solutions: A literature review. Mines Branch Information Circular IC 145, Department of Mines and Technical Surveys, Ottawa, Canada, @ 1963.

4. Sloan, W.J. Ion exchange removal of cyanide values. U.S. Pat. 3 656 893, 1972.

5. Shimamura, I. and Iwano, H. Process for treating waste photographic processing solutions. U.S. Pat. 3 869 383, 1975.

6. Fries, W. Selective separation of cyanide from waste streams by adsorption process. U.S. Pat. 3 788 983, 1974.

7. Avery, N.L. and Fries, W. Selective removal of cyanide from industrial waste effluents with ion-exchange resins. I & EC Product Research and Development, vol. 14, 1975. p. 102.

8. Moore, F.L. An improved ion exchange resin method for removal and recovery of zinc cyanide and cyanide from electroplating wastes. J. Environ. Sci. Health, All (7), 1976. p. 459.

9. Avery, N.L. and Waitz, W.H. Ion exchange treatment process for selective removal of cyanide. Amber-hi-lites, Rohm and Haas, @ 1975.

10. Avery, N.L. Selective removal of iron cyanide anions from fluids containing thiocyanates. U.S. Pat. 4 115 260, 1978.

11. Fries, W. Process for selective removal and recovery of cyanide values by ion exchange. U.S. Pat. 3 984 314, 1976.

12. Gilmore, A.J. The removal of cyanide and metal-cyanide complexes from cyanidation wastes by fixed-bed ion-exchange technology. Mineral Sciences Laboratories Report MRP/MSL (CF) 76-19 (IR), Canada Centre for Mineral and Energy Technology, 1976.

13. Gilmore, A.J. The ion-exchange removal of cyanide from gold-mill wastes for environmental benefit. Mineral Sciences Laboratories Report MRP/MSL (CF) 76-26 (IR), Canada Centre for Mineral and Energy Technology, 1976.

14. Ritcey, G.M. and McNamara, V.M. Treatment of gold mill effluents for removal and recovery or destruction of cyanide - A summary of the joint project with six gold mills. Proceedings of the Tenth Annual Meeting of the Canadian Mineral Processors, Ottawa, January 24 - 26, 1978. p. 152.

15. Trachtenberg, J.J. and Murphy, M.A. Removal of iron cyanide complexes from waste water utilizing an ion exchange process. TMS paper selection LM-79-50, The Metallurgical Society of AIME, @ 1979.

16. Crits, G.J. Cyanide recovery. U.S. Pat. 4 267 159, 1981.

17. Carlson, L.G. Ion exchange treatment for removing toxic metals and cyanide values from waste waters. U.S. Pat. 4 321 145, 1982.

18. Fleming, C.A. Novel process for recovery of gold cyanide from strong base resins. Extraction Metallurgy Symposium, Institute of Mining and Metallurgy, London, September 9-12, 1985.

19. Witte, M.F. Personal Communication.

20. Pourbaix, M. et al. Electrochemical behaviour of arsenic. Potential - pH equilibrium diagrams for the system arsenic - water at 25°C. Technical Report 46, Cebelcor, 1957.

21. Pourbaix, M. et al. Electrochemical behaviour of antimony. Potential - pH equilibrium diagrams for the system antimony - water at 25°C. Technical Report 55, Cebelcor, 1957.

Volume

2

WITTECK DEVELOPMENT INC.
2640 South Sheridan Way, Mississauga, Ontario, Canada L5J 2M4
Telephone: (416) 823-7381 Telex: 06-982328

CONTRACT REPORT NO. 15Q85-00163

GOLD MILL EFFLUENT TREATMENT

UTILIZING ION EXCHANGE TECHNOLOGY

VOLUME II

DSS Contract No. 03SQ.23440-5-9121

Project No. 5152

for

Department of Supply and Services
11 Laurier St.
Hull, Quebec
K1A 0S5

October, 1986

J. L. Laird
Janet L. Laird
Project Metallurgist

M.K. Witte
President

165 pp

0656A

MICROMEDIA

VOLUME II

		PAGE
	APPENDICES	
APPENDIX I	Description of the Literature	A.I.1
APPENDIX II	Analytical Procedures	A.II.1
APPENDIX III	Experimental Results and Procedures	A.III.1
A.III.1.0	Resin Selection: Barren Levels and Breakthrough and Equilibrium Capacities	A.III.2
A.III.2.0	Column I Testwork	A.III.17
A.III.2.1	Background	A.III.17
A.III.2.2	Recovery of HCN from an Acidic Regenerant Solution	A.III.21
A.III.2.3	Elution of Resin Loaded with Metal Cyanide Complexes	A.III.40
A.III.2.4	Elution Isotherms	A.III.44
A.III.2.5	Cyclic Adsorption/Elution Testwork	A.III.47
A.III.2.6	Resin Poisoning Agents	A.III.67
A.III.2.6.1	Adsorption/Elution Testwork using Enriched Cyanide Waste Effluent	A.III.67
A.III.2.6.2	Removal of Iron Cyanides from Strong Base Resins	A.III.75
A.III.2.6.3	Removal of Cobalt Cyanide from Strong Base Resins	A.III.77
A.III.2.7	Removal of Antimony and Arsenic from Mill Effluent using Ion Exchange Resins	A.III.79
A.III.3.0	Column II - Testwork	A.III.95
A.III.3.1	Background	A.III.95
A.III.3.2	Preconditioning Step	A.III.96
A.III.3.3	Cyclic Testwork - Cyanide Levels in Barrens, Breakthrough and Equilibrium Capacity and loss of Copper from Preconditioned Resin	A.III.97
A.III.3.4	Other Forms of Amberlite IRA 400	A.III.109
A.III.4.0	Column I and Column II Operated in Series	A.III.115
APPENDIX IV	Cyanide Recovery and Recycle Questionnaire	A.IV.1
APPENDIX V	References	A.V.1

VOLUME II

LIST OF TABLES

		Page
TABLE 1	Analysis of Composite Feed Samples	A.III.4
TABLE 2	Column I Effluent Analysis; Test 1	A.III.6
TABLE 3	Column I Effluent Analysis: Test 2	A.III.6
TABLE 4	Column II Effluent Analyses; Tests 1 and 2	A.III.7
TABLE 5	Column I Effluent Analysis; Test 3	A.III.10
TABLE 6	Column I Effluent Solution Analysis; Test 4	A.III.11
TABLE 7	Test 2: Recovery of HCN in Alkaline Trap	A.III.27
TABLE 8	Tests 3, 4, 5: Recovery of HCN in Alkaline Traps	A.III.30
TABLE 9	Summary of Testwork on the Recovery of HCN in Alkaline Absorbers	A.III.38
TABLE 10	Optimization of Stripping Process	A.III.41
TABLE 11	Comparison of CANMET and Witteck/Lac Effluents for Recovery of Cyanide and Base Metals from Resin	A.III.47
TABLE 12	Copper Recoveries during Cyclic Testwork, Column I	A.III.51
TABLE 13	Zinc Recoveries during Cyclic Testwork, Column I	A.III.55
TABLE 14	Nickel Recoveries during Cyclic Testwork, Column I	A.III.56
TABLE 15	Iron Recoveries during Cyclic Testwork, Column I	A.III.58
TABLE 16	Cyclic Testwork: Amount of Waste Effluent Treated Concentration of Regenerant Solution	A.III.62
TABLE 17	Cyclic Testwork using Enriched Cyanide Waste Effluent	A.III.69
TABLE 18	Removal of Sb, As, Co, Hg and Mo from Mill Effluent	A.III.73
TABLE 19	Elution Testwork on the Removal of Iron Cyanide Complexes from Strong Base Resin	A.III.76
TABLE 20	Removal of Antimony and Arsenic from Effluent: Tests 1-5	A.III.81
TABLE 21	Removal of Antimony and Arsenic from Effluent using Ion Exchange Resins: Tests 6-9	A.III.83
TABLE 22	Removal of Antimony and Arsenic from Effluent: Test 10	A.III.84
TABLE 23	Removal of Antimony and Arsenic from Effluent: Tests 11 and 12	A.III.86
TABLE 24	Removal of Antimony and Arsenic from Effluent: Tests 13-20	A.III.89

LIST OF TABLFS cont. Page

TABLE 25 Removal of Antimony and Arsenic from Fffluent: Tests 21-24 A.III.90
TABLE 26 Removal of Antimony and Arsenic from Effluent: Tests 25-29 A.III.91
TABLE 27 Removal of Antimony and Arsenic from Effleunt: Tests 30-33 A.III.93
TABLE 28 Cyclic Testwork - Column II A.III.100
TABLE 29 Cycle I: Loading of Column II A.III.105
TABLE 30 Cycle 5: Loading of Column II A.III.106
TABLE 31 Cycle 6: Loading of Column II A.III.107
TABLE 32 Comparison of Breakthrough and Equilibrium Loading Capacities for "CuCN", Sulphate and Hydroxide Forms of Amberlite IRA-400 A.III.113
TABLE 33 Comparison of Breakthrough and Equilibrium Capacity A.III.114
TABLE 34 Cyclic Testwork: Column I Loading Data for Cycle I A.III.117
TABLE 35 Cyclic Testwork: Column I Loading Data for Cycle II A.III.118
TABLE 36 Cyclic Testwork: Column II Loading Data for Cycle I A.III.119
TABLE 37 Cyclic Testwork: Column II Loading Data for Cycle II A.III.120
TABLE 38 Resin Analyses after Two Loading/Stripping Cycles A.III.121

WD1

VOLUME II

LIST OF FIGURES

		PAGE
FIGURE 1	Test 3: Column 1 Loading Isotherms	A.III.12
FIGURE 2	Test 4: Column 1 Loading Isotherms	A.III.13
FIGURE 3	Test 3: Column 2 Loading Isotherms	A.III.15
FIGURE 4	Test 4: Column 2 Loading Isotherms	A.III.16
FIGURE 5	Apparatus used for Test 1 of HCN Recovery Testwork	A.III.22
FIGURE 6	Relative Amounts of HCN and CN^- as a Function of pH	A.III.24
FIGURE 7	Apparatus used for Test 2 of HCN Recovery Work	A.III.26
FIGURE 8	Apparatus used for HCN Recovery Test 3, 4 and 5	A.III.31
FIGURE 9	Recovery of HCN in Alkaline Traps - Tests 3, 4 and 5	A.III.33
FIGURE 10	Apparatus used for HCN Recovery - Test 6	A.III.35
FIGURE 11	Test 6: Amount of Cyanide Recovered in Trap 1 versus Time	A.III.37
FIGURE 12	Apparatus used for Stripping Tests 1 to 3.	A.III.42
FIGURE 13	Stripping Isotherms for Test 1 using 1% Sulphuric Acid Eluant	A.III.45
FIGURE 14	Stripping Isotherms for Test 2 using Witteck/Lac Eluant	A.III.46
FIGURE 15	Stripping Isotherms for Copper and Zinc	A.III.48
FIGURE 16	Cycle 1 Recovery of Cyanide in Caustic Trap	A.III.60
FIGURE 17	Cobalt Recovery from Resin using $NH_4SCN/NaOH$	A.III.78
FIGURE 18	Loading Isotherm for Cycle 1 of Column II Testwork	A.III.102
FIGURE 19	Loading Isotherm for Cycle 5 of Column II Testwork	A.III.103
FIGURE 20	Loading Isotherm for Cycle 6 of Column II Testwork	A.III.104
FIGURE 21	Loading Isotherm for Sulphate, Hydroxide and Cuprocyanide Forms of IRA-400	A.III.111
FIGURE 22	Loading Isotherms for Sulphate, Hydroxide and Cuprocyanide Forms of IRA-400 (semi-logarithmic)	A.III.112

APPENDIX I

Description of the Literature

APPENDIX I

DESCRIPTION OF THE LITERATURE

A literature survey was carried out covering publications and patents relating to the use of ion exchange resins for cyanide recovery. A brief description of each publication is provided.

Throughout the following discussion, the chemistry is described in terms of a divalent metal ion M, and X represents any monovalent anion.

1. Burstall et al (1953)

Burstall et al used a strong base anionic exchange resin to remove gold and base metal cyanide complexes from gold mill effluent, producing a barren solution effectively stripped of all heavy metal cyanide complexes.

A selective elution process is described for the recovery of gold and all base metal cyanide complexes from the resin. A solution of 0.2N HCl elutes nickel and zinc with traces of copper. This is followed by 2N NaCN which elutes iron and copper. Finally, a mixture of acetone with 5% HCl removes gold and silver. Periodic treatment of the resin with 2N KSCN is suggested for removal of cobalt.

For gold barren solutions, the organic strip could be eliminated, or employed periodically to recover traces of gold, which report to the ion exchange cyanide recovery unit.

While this paper describes a method for recovery of base metal cyanide complexes, no process is described for the recovery of free cyanide. Furthermore, a single stripping cycle would be preferable for removal of nickel, zinc and copper from the resin.

2. Goldblatt (1959)

Uranium plants in South Africa use strong base anion exchange resins such as Amberlite IRA-400 for the concentration and recovery of uranium from the leach liquor. There are compounds in solution (such as $Co(CN)_6^{3-}$) which poison the resin, reducing its capacity for uranium and rendering further use of the resin for uranium recovery uneconomical within two years. Thus, there is a large quantity of used resin available for other purposes.

The author reports the results of pilot plant studies on cyanide recovery using the discarded resin from the uranium plant. The method involves the use of two beds of Amberlite IRA-400 resin operating in series. The first bed adsorbs anionic metal cyanide complexes; as described below for a divalent metal M, and any anion X.

$$2Resin^+X^- + M(CN)_4^{2-} \longrightarrow (Resin^+)_2\text{-}M(CN)_4^{2-} + 2X^-$$

The effluent from the first column, containing free cyanide, proceeds to the second column which contains CuCN precipitated within the resin matrix, and adsorbs the free cyanide according to the reaction:

$$Resin^+ + CuCN + CN^- \longrightarrow Resin^+\text{-}Cu(CN)_2^-$$

0656A

WD1

Effluent from the second bed, containing thiocyanate and carbonate, can be returned to the plant as relatively fresh water.

The first bed is stripped using dilute sulphuric acid (1%):

$$(\text{Resin}^+)_2\text{-M(CN)}_4^{2-} + 2H_2SO_4 \longrightarrow (\text{Resin}^+)_2SO_4^{2-} + MSO_4 + 4HCN$$

and periodically with ferric sulphate to remove builtup CuCN precipitate. The eluate, containing metal sulphates and HCN may be passed through a third column of cationic resin to remove the metal cyanides.

$$2\text{Resin}^-H^+ + MSO_4 \longrightarrow (\text{Resin}^-)_2M^{2+} + H_2SO_4$$

The effluent from this third column, containing only HCN and H_2SO_4, may be recycled to the gold plant, or maybe reacidified to 1% H_2SO_4 and used to elute the second column.

The second bed is stripped using dilute sulphuric acid (1%):

$$\text{Resin}^+\text{-Cu(CN)}_2^- + H^+ \longrightarrow \text{Resin}^+ + CuCN + HCN$$

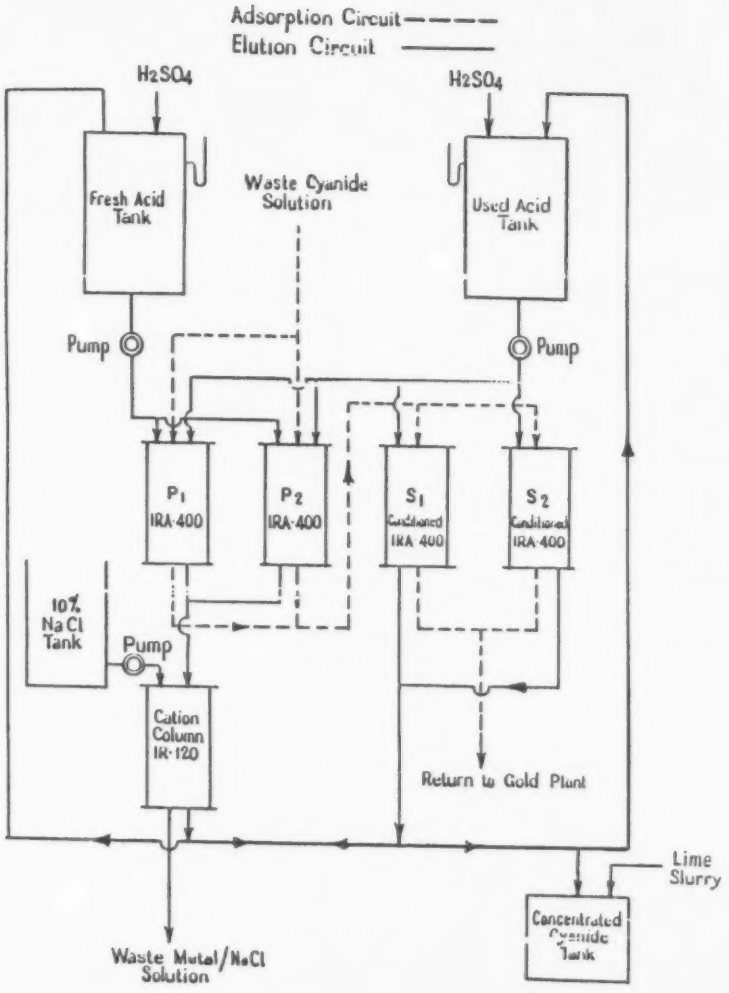
The eluate contains only HCN, and may be recycled to the gold plant.

The third column is stripped using NaCl (10%):

$$(\text{Resin}^-)_2M^{2+} + 2NaCl \longrightarrow 2\text{Resin}^-Na^+ + MCl_2$$

The eluate contains waste metal and proceeds to tailings. This process is summarized in the flow sheet shown overleaf.

0656A



This process recovers both free and complexed cyanide as HCN. The author reported 95.6% cyanide recovery, and 97.9% cyanide recovery when the resin was regenerated using ferric sulphate.

One problem with this method is that leakage of cyanide from the second bed is usually high, because the precipitated CuCN occludes the pores of the resin, inhibiting the penetration of the waste solution into the resin.

0656A

WD1

3. Gilmore et al (1963)

This early review of the prior literature reviewed both the acidification and ion exchange method of cyanide recovery. Using information obtained from operating gold mills, the reviewers concluded that both processes would be uneconomical in most Canadian operations, due mainly to the small tonnages of cyanide discarded.

The advantages of the ion exchange process, first proposed by Goldblatt (1959), which were particularly attractive to South African applications were listed as:

1. Removal of temporary poisons from uranium plant resins, allowing their reuse in uranium plants.

2. Recycling of the secondary column effluent to the gold extraction plant, thereby reducing water consumption.

3. The relatively high concentration of base metals in the cyanide waste solutions which can be recovered by ion exchange.

However, at the time of this review there was little concern regarding water supply in Canada, the source of used resin at uranium producing centres was at some distance from the gold producing area, and the poisoning of the resin was not as serious in Canadian uranium operations, as it was in South African plants. Both processes required the daily recovery of 230 kg equivalent NaCN to break even (at 1963 prices), and at the time few gold mining operations in Canada met this requirement.

0656A

WD1

The authors concluded that cyanide recovery by ion exchange would be uneconomical in most Canadian plants. However, the ion exchange process was deemed more generally applicable than acidification since its costs are not dependent on the concentration of cyanide in solution, but only on the total daily tonnage.

4. Sloan (US Pat 3 656 893; 1972)

This patent describes the recovery of free and complexed cyanide values from a waste solution using a mixed bed of cationic (H^+ form) and weakly basic anionic (free base form) resins. The free cyanide is complexed by the addition of sufficient metal ions, such as Cu^+, Ni^{2+}, Ag^+, Au^+ or Cd^{2+}. The solution is passed through the mixed resin bed, where the sodium and/or potassium salts of the metal cyanide complexes are converted to their corresponding acids and adsorbed onto the weak base resin:

$$\text{Resin-COOH} + \text{Resin-NR}_2 + \text{NaCu(CN)}_2 \longrightarrow \text{Resin-COONa} + \text{Resin-NR}_2\text{H}^+\text{Cu(CN)}_2^-$$

The weak base resin is stripped and regenerated using base:

$$\text{Resin-NR}_2\text{H}^+\text{Cu(CN)}_2^- + \text{NaOH} \longrightarrow \text{Resin-NR}_2 + \text{NaCu(CN)}_2 + \text{H}_2\text{O}$$

The cationic resin is regenerated using acid:

$$\text{Resin-COONa} + \text{H}^+ \longrightarrow \text{Resin-COOH} + \text{Na}^+$$

0656A

WD1

Using copper to complex free cyanide, the author reports a loading of 0.88 milliequivalents of copper per mL of weak base resin (IRA-93), and essentially complete removal of all copper from the resin when stripping with 10% NaOH. All cyanide is recovered in the metal complex form. No method is given for recovery of cyanide in a reusable form.

5. Shimamura et al (US Pat 3 869 383; 1975)

This patent teaches the removal of ferricyanide and ferrocyanide from waste solutions (pH 7 to 9) using weakly basic anionic exchange resins in the free base form in the presence of a compound having a buffering action at a pH of 7 to 9. This process would be of interest if iron is considered as a complexing agent for free cyanide. The resin is stripped of the ferricyanide and ferrocyanides and regenerated to the free base form using sodium hydroxide. The concentrated iron cyanide solution may then be purified by conventional techniques such as precipitation as Prussian blue by the addition of iron salts, by electrodialysis, by reverse osmosis, or by combustion or pyrolysis. This process is claimed to work well for solutions containing 2000 ppm $Fe(CN)_6^{4-}$ plus $Fe(CN)_6^{3-}$, and produces concentrated solutions containing up to 10,000 to 100,000 ppm total $Fe(CN)_6$. The reduction in ion exchange capability of the regenerated resin is claimed to be extremely small. This process, developed primarily for the treatment of waste photographic processing solutions, is less applicable to the gold industry because of the large salt background which reduces the capacity of the weak base resin and increases the chemical requirements for regeneration.

Also, the amount of cyanide and the form of the cyanide in the product solution is identical to that of the original stream; the solution has been concentrated only. If the solution may be recycled as is, as in the photographic industry, this is a suitable process. However, in gold treatment plants, free cyanide is desired.

6. Fries (US Pat 3 788 983; 1974) and

7. Avery and Fries (1975)

These two papers deal with the complexation method of converting free cyanide to metal cyanide complexes by the addition of a metal cation, followed by recovery of all anions by ion exchange. The most troublesome problem with this method is stated to be the requirement of stoichiometric addition of the metal ion:

$$M^{2+} + 4CN^- \longrightarrow M(CN)_4^{2-}$$

The addition of insufficient metal ion allows the leakage of free cyanide through the column:

$$M^{2+} + 8CN^- \longrightarrow M(CN)_4^{2-} + 4CN^-$$

whereas the addition of excess metal ion produces nonionic metal cyanide complexes which will not adsorb onto anionic resins, and will precipitate:

$$M^{2+} + 2CN^- \longrightarrow M(CN)_2$$

Furthermore, the addition of an excess of metal ion in the presence of $M(CN)_4^{2-}$ can convert the ionic species to the nonionic species.

$$M^{2+} + M(CN)_4^{2-} \longrightarrow 2M(CN)_2$$

The automated addition of stoichiometric amounts of M^{2+} to a stream which flucuates in cyanide content is not feasible.

The authors use ferrous ion as a complexing agent for cyanide, followed by adsorption employing a weakly basic anion exchange resin in the acid salt form:

$$Fe^{2+} + 6CN^- \xrightarrow{pH > 9} Fe(CN)_6^{4-}$$

$$4\text{Resin-}NR_2H^+X^- + Fe(CN)_6^{4-} \xrightarrow{pH\ 4\ to\ 7} (\text{Resin-}NR_2H^+)_4Fe(CN)_6^{4-} + 4X^-$$

The advantage of ferrous ion over other divalent metal ions is that the ferrocyanide complex is stable with respect to further reaction with excess metal ion. Excess ferrous ion is precipitated quantitatively as ferrous hydroxide at the pH of complex formation. The ferrocyanide complex is stable at all pH values and is effectively adsorbed by weakly basic resins operating in the acid salt form. Most other metal cyanide complexes are not as stable at the pH levels (pH 4 to 7) required to maintain the resin in the acid salt form. Operation in the acid salt form of the resin increases the loading capacity of the resins with respect to the free base form.

0656A

WD1

The weakly basic resin is easily stripped by the addition of base:

$$(\text{Resin-NR}_2\text{H}^+)_4\text{Fe(CN)}_6^{4-} + 4\text{OH}^- \longrightarrow 4\text{Resin-NR}_2 + \text{Fe(CN)}_6^{4-} + 4\text{H}_2\text{O}$$

producing a highly concentrated Fe(CN)_6^{4-} solution. The resin is converted back to the acid salt form by treatment with sulphuric acid.

The authors report removal of cyanide to levels of < 1 ppm from streams containing up to 2000 ppm, and loading capacity of the resins to be of the order of 20 to 30 mg CN/mL resin.

Although the weakly basic resin in the acid salt form is said to be as selective for ferrocyanide as strongly basic resins, even in the presence of a high inorganic salt background, the waste solution must be acidified to pH 4 to 7 prior to loading the column. This would require copious amounts of acid, and would decompose most other metal cyanide complexes. The weakly basic resin is readily stripped using dilute sodium hydroxide, but then must be reconverted to the acid salt form by pH adjustment. The free cyanide is recovered as $\text{Na}_4\text{Fe(CN)}_6$ or as $\text{Fe}_4[\text{Fe(CN)}_6]_3$, Prussian blue, by the addition of ferric ions to the spent stripping solution. The sodium hydroxide solution must be acidified to encourage formation of the precipitate, but once formed the precipitate is stable. The alkaline stripping solution however is destroyed and cannot be reused.

8. Moore (1976)

This paper also describes the use of weakly basic anionic exchange resin for the recovery of free and complexed cyanide (Amberlite XE-275, tertiary amine functionality with a crosslinked acrylic matrix). In this case, zinc cyanide and free cyanide were recovered from waste electroplating solutions.

0656A

When the feed effluent was pH 7, leakage during the absorption cycle was less than 0.03 mg/L for zinc, and less than 0.1 mg/L for cyanide. This increased to < 0.5 mg/L for zinc cyanide and 1 to 3 mg/L for cyanide when the pH of the feed solution was increased to pH 8.3. The author recommended feed solutions in the range of pH 6 to 7.5 for this process.

The loaded resin was stripped efficiently using 2M NaOH. The zinc cyanide and cyanide recovered during stripping can be recycled for use in the electroplating plant. After stripping the resin must be reconverted to the acid salt form prior to reuse.

While the method works well for electroplating solutions, the pH requirement of the feed solution prohibits its use for gold mill effluent solution.

9. Avery and Waitz (@ 1975) and

10. Avery (US Pat 4 115 260; 1978)

The process is similar to that proposed by the same group in the patent and paper described above (6, 7). The major difference is that Amberlite XE-279, an acrylic, strongly basic anion exchange resin is employed, rather than a weakly basic resin in the acid salt form.

The free cyanide is complexed using an excess ferrous ion:

$$2Fe^{2+} + 6CN^{-} \xrightarrow{-OH} Fe(CN)_6^{4-} + Fe(OH)_2$$

0656A

The ferrocyanide is adsorbed onto the strongly basic resin in the chloride form.

$$4\text{Resin-}NR_3^+Cl^- + Fe(CN)_6^{4-} \longrightarrow (\text{Resin-}NR_3^+)_4Fe(CN)_6^{4-} + 4Cl^-$$

The resin may be stripped and regenerated in a single step using 15% sodium chloride

$$(\text{Resin-}NR_3^+)_4\ Fe(CN)_6^{4-} + 4\ NaCl \longrightarrow 4\text{Resin-}NR_3^+Cl^- + Na_4Fe(CN)_6^{4-}$$

The iron cyanide complex may be recovered from the salt solution by the addition of ferric chloride

$$3Na_4Fe(CN)_6 + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12\ NaCl$$

The advantages of using a strongly basic resin over a weakly basic resin in the acid salt form are: (a) A high loading capacity is achieved without prior adjustment of the feed solution and the resin to pH 4 to 7, (b) The stripping and regeneration process involves a one step treatment with NaCl, rather than a two step treatment of stripping with NaOH followed by regeneration of the resin using dilute acid; (c) Sodium chloride is safer and less expensive than sodium hydroxide; (d) The ferrocyanide may be recovered from the NaCl regenerate solution by the addition of $FeCl_3$ (to form $Fe_4[Fe(CN)_6]_3$), no pH adjustment is necessary as in the case of NaOH; (e) The spent regenerate may be reused, whereas, the spent NaOH has been destroyed by the pH adjustment step.

Since strongly basic resins are efficient over a wide pH range, this process may be used to treat alkaline or acidic fluids without pH adjustment. If the feed solution is alkaline, the excess ferrous ion added may be removed as $Fe(OH)_2$ precipitate prior to contacting the feed solution with the resin.

0656A

WD1

If the feed solution is acidic, the excess ferrous ion will be removed from the resin with the NaCl regenerant. After the iron cyanide complex is recovered as Prussian blue by the addition of ferric chloride, the excess iron may be recovered as $Fe(OH)_2$ by increasing the pH.

This process, employing Amberlite XE-279, a strongly basic acrylic anionic exchange resin, is superior to methods previously reported using strongly basic polystyrene anionic resins since the acrylic resins show a greater selectively for iron cyanides over thiocyanate, as well as a greater resistance of organic fouling. Amberlite XE-279 is said to have a capacity of up to 2.3 lb CN per cu ft of resin, and shows no loss in performance after 91 loading and regeneration cycles.

Although this process works very well for solutions containing ferrocyanides and free cyanide in the presence of thiocyanate, most other base metals, if present, would not be eluted efficiently from the resin using NaCl, and a multielution process would have to be adopted.

11. Fries (US Pat 3 984 314; 1976)

This patent teaches the complexation of free cyanide using an excess of copper (II), followed by adsorption onto a strongly basic resin

$$4\ CN^- + Cu^{2+} \xrightarrow{pH\ 9} Cu(CN)_4^{2-}$$

$$Cu(CN)_4^{2-} + Resin\text{-}NR_3^+ \longrightarrow (Resin\text{-}NR_3^+)_2Cu(CN)_4^{2-}$$

Any excess Cu^{2+} may be recovered by contacting the eluate with a cationic exchange resin:

$$2Resin^{-}H^{+} + Cu^{2+} \longrightarrow (Resin^{-})_2Cu^{2+} + 2H^{+}$$

The anionic resin may be stripped and regenerated using 8N HCl:

$$(Resin\text{-}NR_3^{+})_2Cu(CN)_4^{2-} + 4HCl \longrightarrow 2Resin\text{-}NR_3^{+}Cl + CuCl_2 + 4HCN$$

The author reports 100% recovery of cyanide and 81% recovery of the copper in the regenerant solution.

No mention is made in this patent of the ease with which Cu^{II} reacts to give Cu^{I} in the presence of cyanide ions

$$2Cu^{2+} + 4CN^{-} \longrightarrow 2CuCN + C_2N_2$$

The CuCN will precipitate within the resin matrix, and is much more difficult to remove than $Cu(CN)_4^{2-}$.

12. Gilmore (1976a)

Inspired by an Environment Canada tentative objective of 0.1 ppm total cyanide in cyanidation effluents to the environment, this CANMET study reports the results of a feasibility study to remove and recover cyanide and base metals from cyanidation waste effluents. The method for the laboratory scale study was essentially the process piloted by Goldblatt in 1959. The waste cyanide solutions were passed through two columns in series. The first column, containing the strongly basic anionic exchange resin Amberlite IRA-400 in the sulphate form, was to remove all anionic metal cyanide complexes.

The second column, containing Amberlite IRA-400 in the sulphate form, with CuCN precipitated within the resin matrix, was to remove free cyanide. After passing through these two columns, the waste solution should meet proposed guidelines for cyanide and heavy metals, i.e., 0.1 ppm CN; 0.3 ppm Cu; 0.5 ppm Ni and 0.5 ppm Zn.

The primary column was stripped using 1% H_2SO_4, and the resulting effluent, containing metal sulphate complexes, was passed through a cationic exchange resin. The secondary column was stripped using 1% H_2SO_4. The cationic column was stripped using sodium chloride. The equations for this process are summarized below.

Primary Column

Loading: $\text{Resin-}SO_4^{2-} + M(CN)_4^{2-} \longrightarrow \text{Resin-}M(CN)_4^{2-} + SO_4^{2-}$

Stripping: $\text{Resin-}M(CN)_4^{2-} + 2H_2SO_4 \longrightarrow \text{Resin-}SO_4^{2-} + MSO_4 + 4HCN$

Secondary Column

Loading: $\text{Resin-}Cu(CN)_3^{2-} + CN^- \longrightarrow \text{Resin-}Cu(CN)_4^{3-}$

Stripping: $\text{Resin-}Cu(CN)_4^{3-} + H_2SO_4 \longrightarrow \text{Resin-}Cu(CN)_3^{2-} + HCN + HSO_4^-$

Cationic Column

Loading: $2\text{Resin-}Na^+ + MSO_4 \longrightarrow (\text{Resin})_2\text{-}M^{2+} + Na_2SO_4$

Stripping: $(\text{Resin})_2\text{-}M^{2+} + 2NaCl \longrightarrow 2\text{Resin-}Na^+ + MCl_2$

0656A

WD1

Six different cyanide waste solutions were tested, ranging in total cyanide and base metal concentrations as summarized in the following table.

Analysis, ppm	A	B	C	D	E	F
CN, total	17-32	740-760	76-94	410-470	280-320	230-240
CN, free	6-9	225-240	33-44	200-240	190-200	160-230
Cu	12-13	13-15	28-35	240-250	77-83	16-19
Ni	2	20	8-10	0.7-9	6	3
Zn	4-6	50-62	17-23	72-76	93-96	12-13

A summary of the results of the test work is provided below.

Solution:	A	B		C	D		E		F
Column:	SO_4	CuCN	Scav.	SO_4	SO_4	Scav.	SO_4	Scav.	CuCN
CN, total	<0.1	0.73	<0.1	<0.1	43	<0.1	<0.1	<0.1	<0.1
Cu	<0.05	2	<0.01	0.02	1	-	<0.02	-	0.1
Ni	<0.2	<0.02	<0.03	0.02	<0.03	-	<0.03	-	<0.06
Zn	<0.08	0.06	<0.01	<0.02	0.07	-	<0.01	-	0.02

For the waste solution A, C, and E containing from 17 to 320 ppm cyanide, both the free and heavy metal cyanide complexes were adsorbed by the primary column. The environmental guidelines (<0.1 ppm CN_T; <0.3 ppm Cu; <0.5 ppm Ni; <0.5 ppm Zn) were attained up until breakthrough, which varied according to the flowrate and cyanide concentration in the waste solution. For these three tests, the initial stages of adsorption on the secondary column were accompanied by leakage of cyanide from the secondary CuCN column ($\sim$ 1 ppm CN_T). The author concluded that the influent concentration of free or complexed cyanides dissolved or displaced the CuCN on the secondary column.

0656A

WD1

Following this initial period, which lasted for 120 to 180 bed volumes, the effluent from the secondary column also achieved the government guidelines until breakthrough. For these three solutions, the author recommended operation with one SO_4 column (solution A) or series loading with two SO_4 columns (solutions C and E) as being more effective in attaining a sustained effluent containing 0.1 ppm CN_T. To test this prediction using solution E, a composite effluent from the primary column was passed through a scavenger SO_4 column. The cyanide was reduced from 27 ppm CN_T and 26 ppm CN_F to <0.1 CN_T.

For solutions B and D, containing higher levels of CN_T in the waste solution, $\sim$ 750 and $\sim$ 440 ppm CN_T, respectively, the primary SO_4 column did not attain government guidelines by itself. However, the CuCN on the secondary column appeared to dissolve during loading, producing an effluent containing both cyanide and copper, (see table above.) When effluent from the CuCN column (solution B) was passed through a scavenger SO_4 column, the cyanide concentration was reduced from 0.73 to <0.1 ppm, and the copper concentration was reduced from 2 to <0.01 ppm. When the effluent from the primary SO_4 column (solution D) was passed directly through a scavenger SO_4 column, the cyanide concentration was reduced from 43 to <0.1 ppm. However, the same solution, after passage through the secondary CuCN column, contained 0.37 ppm CN_T. The scavenger SO_4 column performed better than the CuCN column.

For the last solution, F, the CuCN on the secondary column was again stripped during loading. After this initial stage, the effluent from the secondary CuCN column achieved <0.1 ppm CN_T up until breakthrough. Although these two columns in series did achieve government guidelines, recycling the initial effluent from the secondary CuCN column was not deemed to be a viable operation.

0656A

WD1

In summary, Gilmore concluded that for most the solutions, the SO_4 form of the column was adequate by itself for lowering the cyanide and base metals to the desired levels, and recommended one or two such columns in series. Cyanide loadings of 2 to 4 lb of CN/cu ft of resin were attained for the primary column. The heavy metals were recovered as a high grade metal oxide, 98% ZnO + NiO + CuO.

Stripping the primary column with 1% H_2SO_4 is advantageous, since H_2SO_4 is inexpensive and readily available near gold operations. All the cyanide is recovered as HCN in caustic media.

In addition to reducing cyanide and base metal levels to within Environment Canada objectives, and recovering both for further use, thiocyanate is also removed to $<$1 ppm.

13. Gilmore (1976 b)

In a subsequent report, the process was scaled up to a continuous operation. One cyanide leach liquor was studied. The resin loading on the first cycle was 2 lb CN/cu ft of resin; 1.5 lb CN/cu ft was proposed to allow for a safety margin in plant operation. Metal loading on the cationic bed averaged 0.55 lb/cu ft of resin. Desorption of the cyanide from the strongly basic anionic column required 15.3 lb H_2SO_4/lb CN. Desorption of metals from the cationic column required 0.56 lb NaCl/lb CN.

14. Ritcey and McNamara (1978)

This summary report describes work carried out by various investigators at CANMET on three cyanide recovery technologies, acidification, ion exchange, and alkali chlorination, and compares them along with data published by other workers on a fourth process, ozonation.

Within this report, Ritcey describes unpublished work by Lucas on continuous fluidized - bed ion exchange. This process was investigated since it has the advantage of handling any solids present in the feed effluent, allowing for a smaller inventory of resin, and therefore lower capital costs. Using only the sulphate form of Amberlite IRA-400, the feed liquor flow rate was adjusted to determine the optimal residence time and flow rate required to maintain 0.1 ppm CN_T in the effluent. The optimal conditions were tested in a continuous pilot plant campaign. A retention time of 3.5 h was used at a flow rate of 150 gal/h/sq ft Using a H_2SO_4 concentration of 4.5 volume percent in the stripping process, and a NaOH wash solution of pH 13, a stripping efficiency of 94% was achieved, while the raffinate contained 0.9 mg/L CN_T.

When using a single stage continuous ion exchange process, resin loading can not exceed 20% in order to obtain the desired raffinate. Elution and washing must be 99% efficient and fast in order to maintain small volumes of resin. However, the CIX unit required 723 cu ft of resin to treat 125 gpm of 36 ppm CN_T solution through a CIX unit, whereas 200 cu ft of resin were required to the same solution through a static bed ion exchange pilot plant.

A major problem with this method is the possibility of precipitating metals, in particular copper, within the resin bed.

15. Trachtenberg and Murphy (@ 1979)

This paper provides operating parameters for reducing cyanide levels, present as ferri and ferrocyanides, from waste solution using anion exchange technology, and would be of particular interest if iron is considered as a complexing reagent for free cyanide.

A strongly basic anionic resin (Amberlite XE-279) for the testwork, since the pH of the waste solution would not need to be adjusted prior to contact with the anion exchange resin, and since the resin could be stripped and regenerated using 15% NaCl in a single step.

Test runs were conducted until breakthrough occurred. Flowrate through the column and the influent cyanide concentrations were found to effect the effluent cyanide concentration. Approximately 1 ppm cyanide (as iron cyanide complexes) in the effluent could be achieved when the influent cyanide concentration was $\leqslant$ 365 ppm by maintaining a flowrate of $\leqslant$ 1.0 gal/min/cu ft of resin. Faster flowrates could be employed when operating at lower influent cyanide concentrations.

Regeneration of the resin was achieved by passing 15% NaCl through the column for 2 hours at 0.25 gal/min/cu ft of resin. Concentrations of 10 000 $\pm$ 500 ppm cyanide were obtained in the regenerant during the first hour of elution, equivalent to approximately 95% of the iron cyanide complexes. Eluent from the second hour contained $<$ 500 ppm cyanide, and could be recycled as an economy measure.

0656A

WD1

16. Crits (US Pat 4 267 159; 1981)

This patent describes the separation of free and complexed cyanides from cyanide waste effluent using a type II strong base resin (ie, functional group is dimethylethanolamine rather than trimethlyamine typical of type I strong base resins). Whenever leakage of free cyanide from the column exceeds the tolerable limit for discard to the environment (0.1 ppm), loading is stopped, and free cyanide is stripped from the column using a weakly alkaline or salt solution (NaOH, $Ca(OH)_2$ or NaCl). The resulting alkaline cyanide solution may be recycled to the mill. Periodically, stronger alkaline solution is used to remove metal cyanide complexes from the resin. The resulting solution containing complexed cyanides may be treated for cyanide destruction.

Typical feeds for this invention were stated to be 15 to 60 ppm free cyanide, 2 ppm Zn, 1 ppm Cu and 0.5 ppm Fe. The modal leakage of free cyanide from the column during loading was 0.1 ppm, although the average leakage was 0.8 ppm.

This process has the advantage of stripping and regenerating the resin in a single step using sodium hydroxide or lime, unlike most strong base resins. However, it claims to work well even when lime is present in the feed solution, even though dilute lime is employed to strip the free cyanide from the column during regeneration. Although, the authors reduce the cyanide concentration to 1 ppm, the method would not be expected to work as efficiently when higher concentrations of metal cyanide complexes are present in the feed solution. Under conditions of interest to the present investigation, metals concentrations in solution could be as high as 50-200 ppm Cu, Fe and/or Zn.

0656A

Cyanide would not load as efficiently in the presence of such high concentrations metal cyanide complexes, and free cyanide breakthrough would occur much sooner.

17. Carlson (1982)

This patent describes the removal of toxic metal cyanide and free cyanide from waste waters by means of a multi-level ion exchange resin bed. The waste effluent, in this case from electroplating baths, is passed through a strong base anionic exchange resin layer, a weak acid cationic exchange resin layer, and finally a strong acid cationic exchange layer. This process reportedly removes the heavy metal cyanide complexes and the free cyanide from solution. Cationic metals would be removed by the cationic resin beds.

Stripping was carried out using acid. The cyanide is recovered as hydrocyanic acid and trapped in a caustic solution as NaCN.

Sodium hydroxide is used to regenerate the first two resin layers. The anionic exchange resin is converted to the hydroxide form, the weak acid resin is converted to the sodium form. The strong acid cationic resin remains in the hydrogen ion form.

A special cyanide recovery unit is described for the trapping of cyanide as the sodium salt. Temperatures of 180 degrees F resulted in removal of 80% of the hydrocyanic gas; at 200 degrees F all of the HCN was removed from the acidic regenerant solution within one hour. The caustic solution trapped cyanide efficiently up to 380 g/L NaCN.

Once again, while the process works efficiently for electroplating waste effluents, it would not apply to the treatment of gold mill effluent solution. The free cyanide present would not load efficiently on the strong base anionic exchange resin layer in the presence of multivalent metal cyanide complexes.

0656A

APPENDIX II

Analytical Procedures

APPENDIX II

ANALYTICAL

All solution analyses were performed in-house. Base metals (Cu, Fe, Ni, Zn, As, Sb, Co, Mo, Pb) were assayed directly either by Atomic Absorption or Direct Current Plasma (DCP). Low level arsenic (less than 0.5 ppm) was assayed colourimetrically using pyridine/silver diethyldithiocarbamate reagent after HCl/Zn arsine evolution.

Thiocyanate was assayed colourimetrically using ferric nitrate. Total cyanide was assayed using the hydrochloric acid/hydroxylamine hydrochloride distillation method and finished colourimetrically with isonicotinic acid/barbituric acid. Low level free cyanides (less than 5 ppm) were assayed colourimetrically as described above. Free cyanide (greater than 5 ppm) were titrated with silver nitrate reagent using Rhodanine B indicator.

Resins were acid digested and assayed as above for base metals. Resins were assayed for cyanide by distillation as described above.

APPENDIX III

Experimental Results and Procedures

APPENDIX III

EXPERIMENTAL RESULTS AND PROCEDURES

The testwork on the two column system was subdivided in four general areas. In the first section, Appendix III Section 1.0, the results of the initial resin selection testwork are reported. The comparison was made on the basis of barren levels and breakthrough and equilibrium capacities for column I and column II. After the initial selection, the operation of each column of the two column system was investigated separately.

The results of the testwork performed on column I, for the removal of base metal cyanide complexes from effluent solution, are reported in Appendix III Section 2.0. This section provides the results of the reinvestigation into stripping procedures, the percent cyanide recoverable in various types of alkaline traps, cyclic testwork involving twenty adsorption/elution cycles, the results of an investigation into potential resin poisoning agents, and the results of an investigation into the removal of arsenic and antimony using ion exchange resin.

The results of the analogous program for column II, for the removal of uncomplexed or free cyanide from mill effluent, are provided in Appendix III Section 3.0. This section includes the results of six adsorption/elution cycles, including barren levels, breakthrough capacities and loading isotherms, a reinvestigation into the preconditioning step as well as an investigation into the frequency of reconditioning the cuprocyanide form of the resin. In addition, testwork was performed on other forms of anionic exchange resins to determine if there is a form better able to remove free cyanide from gold mill effluent.

0656A

WD1

Finally, the two columns were coupled and operated in series during the last phase of the testwork. These results are provided in Appendix III Section 4.0. All elements present in the feed effluent are followed during a two cycle study of the two columns operating in series.

A.III.1.0 RESIN SELECTION: BARREN LEVELS AND BREAKTHROUGH AND EQUILIBRIUM CAPACITIES

The CANMET report by A.J. Gilmore (12) tested the Goldblatt (2) two column system for cyanide removal and recovery. Both Goldblatt and Gilmore used Amberlite IRA-400, a gel type strong base anionic exchange resin, in the sulphate form for column I, and in the sulphate form preconditioned with copper cyanide for column II. This resin was included in the current test program, along with Lewatit MP-500, a strong basic macroporous resin, for comparison. It was anticipated that the macroporous resin might show similar loading capacities and barren levels, but display a higher degree of physical strength.

Weak base resins were not investigated due to their lower loading capacities at the pH levels typical of gold mill effluent solutions (pH 9 to 11.5).

The initial comparison of the two strong base resins, Amberlite IRA-400 and Lewatit MP-500, was carried out by determining barren levels and breakthrough capacities for the two columns operating in series. The first column contained the sulphate form of the resin. The effluent from the first column proceeded directly to the second column which contained the same resin, but preconditioned with a solution of cuprocyanide according to the method by Goldblatt (2).

Two different mill effluent solutions were tested. Therefore, four tests were carried out in all. The procedures followed are described below.

The appropriate anionic exchange resin (Amberlite IRA-400 or Lewatit MP-500 in the sulphate form; 50 mL) was placed in the first column (2 cm diameter). The same resin (50 mL), but preconditioned with copper cyanide, was placed in the second column (2 cm diameter). The resin beds in both columns were rinsed with distilled water. Gold mill effluent was fed through the two columns in series at a flow rate of 12.5 mL/min or 0.25 bed volumes (BV) per minute for a retention time of 1.6 minutes. This flow velocity (3.1 $mL/cm^2/min$) is analogous to the flow velocities used in the original work by CANMET utilizing similar mill effluent solutions.

All samples taken were measured for pH and stabilized to $pH \geq 12$ using sodium hydroxide pellets. Column feed solution was sampled twice daily and combined to form one composite feed sample for each test. Composite feed samples were assayed for Cu, Fe, Ni, Zn, SCN and CN(t). Columns were operated on a 8 hour/day basis.

Small samples were taken from the column I effluent; the bulk of the solution proceeded to the second column. Since the function of the primary column is to remove base metal cyanide complexes, the column I effluent samples were assayed for Cu, Fe, Ni and Zn.

For the first two tests, using effluent B, adsorption was terminated when metals breakthrough was attained, to determine the breakthrough or operating capacity and in order to avoid contamination of the secondary column with base metal cyanide complexes.

0656A

This would be desirable in a full scale operation, in order to avoid treatment of the secondary column eluate for base metals after the elution cycle, and to limit resin poisoning to the primary column, with its inherent special elution treatment. For the first two tests, composite samples of the secondary column effluent were assayed for copper and total cyanide.

For the second two tests, using effluent A, adsorption was continued until full equilibrium capacity was attained for at least one of the metals, in this case copper, in order to determine equilibrium capacities and to produce complete loading isotherms for column I. Individual samples of column II effluent were assayed for total cyanide to produce a loading isotherm for the second column as well.

The barren feed analyses for each test is provided in Table 1 below, along with the type of resin and feed used for each test.

Table 1

ANALYSIS OF COMPOSITE FEED SAMPLES

Test	Resin	Barren Feed	Barren Feed Analysis, ppm						
			Cu	Fe	Ni	Zn	SCN	CN(t)	pH
1	MP-500	B	65	14.3	45.0	61	230	615	10.7
2	IRA-400	B	68	15.1	49.0	66	315	657	10.7
3	IRA-400	A	196	2.81	4.70	110	560	435	11.6
4	MP-500	A	249	5.42	5.30	143	690	519	11.5

The results of the four tests are discussed below.

Tests 1 and 2; Using Effluent B

The column I effluent assays for base metals are provided in Tables 2 and 3 for tests 1 and 2, respectively. Loading was terminated when the base metals assay in the column I effluent attained 0.1 mg/L for one or more of the base metals. The original CANMET report stated the objective of removing heavy metals to the range of less than 0.01 to 0.07 ppm for Cu, Ni and Zn.

As can be seen from the data provided in Tables 21 and 22, the two resins tested, Lewatit MP-500 and Amberlite IRA-400, displayed comparable breakthrough capacities, showing breakthrough (greater than 0.1 ppm) for nickel first, after 70 bed volumes, followed by copper, iron and zinc.

Since there were no base metal cyanides reporting to column II, column II effluent was assayed only for CN(t), as well as for copper. Copper was included during the initial bed volumes in order to determine if leakage of copper from the preconditioned resin may present a problem, either from an environmental point of view, or in terms of the required frequency of reconditioning the cuprocyanide form of the resin.

The results of the column II effluent analyses are provided in Table 4 for tests 1 and 2. Composite samples of the column effluent were assayed for CN(t) and Cu. For both tests 1 and 2, the cyanide content of the first 65 bed volumes of effluent was below the detection limit for total cyanide, 0.02 ppm. Although this does not rule out the possibility of a brief period of higher cyanide levels in the column effluent, it does imply that if mixed, in a polishing pond for example, a composite of the first 65 bed volumes for either type of resin, would achieve the target of less than 0.1 ppm CN(t).

0656A

WD1

Table 2

COLUMN I EFFLUENT ANALYSIS; TEST 1

(MP-500 USING EFFLUENT B)

Bed Volumes	Column I Effluent Analysis, ppm				pH
	Cu	Fe	Ni	Zn	
10	0.09	<0.005	0.05	0.05	10.4
20	0.07	<0.005	0.03	0.04	10.6
30	0.06	<0.005	0.02	0.06	10.6
50	0.06	<0.005	0.03	0.04	10.8
70	<0.01	0.03	0.10	0.05	10.8
90	0.12	0.13	0.11	0.07	10.7

Table 3

COLUMN I EFFLUENT ANALYSIS; TEST 2

(IRA-400 USING EFFLUENT B)

Bed Volumes	Column I Effluent Analysis, ppm				pH
	Cu	Fe	Ni	Zn	
10	0.10	<0.005	0.03	<0.006	10.5
20	0.05	<0.005	0.05	<0.006	10.5
30	0.05	<0.005	0.03	<0.006	10.6
50	0.05	<0.005	0.03	<0.006	10.6
70	<0.01	0.02	0.11	0.01	10.7
90	<0.01	0.04	0.10	0.01	10.7

Table 4

COLUMN II EFFLUENT ANALYSES; TESTS 1 AND 2
(EFFLUENT B)

Effluent Bed Volumes	Column II Effluent Analyses, ppm			
	Test 1; MP-500		Test 2; IRA-400	
	CN(t)	Cu	CN(t)	Cu
1-24	<0.02	0.33	<0.02	0.35
25-65	<0.02	0.33	<0.02	1.11
74	40	-	1.0	-
79	165	-	15.5	-
89	-	-	380	-

0656A

Amberlite IRA-400 showed better breakthrough capacity for cyanide, reaching 1 mg/L CN(t) after 74 bed volumes. At this stage the MP-500 resin had already leaked cyanide to 40 mg/L.

However, copper leaked from the secondary column. At this stage it was decided to investigate fully the problems which might result from utilizing a column preconditioned with a base metal cyanide complex, in particular, the leakage of the base metal from the resin during adsorption. (See Section 5.3).

It should be noted that while the primary column was loaded only to breakthrough, or operating capacity after ninety bed volumes, the secondary column, which contained the same quantity of resin, was halfway to equilibrium capacity. In a full scale operation, either larger columns would be required for the secondary columns, or they would have to be regenerated more frequently than the primary columns.

Tests 3 and 4; using Effluent A

As mentioned above, loadings for tests 3 and 4 were continued until the metals assay in the column I effluent approached that in the feed solution for at least one of the metals. Although this resulted in base metal cyanides reporting to the secondary column, it provided the required information to produce loading isotherms for both the primary and secondary columns. The data for the primary columns are presented in Tables 5 and 6 as well as Figures 1 and 2 .

First, considering the breakthrough capacity data in Tables 5 and 6, copper broke through first for both resins, as opposed to nickel, as was observed for effluent B. This is due to the copper levels in feed solution being so much higher than the other base metals. Base metals in effluent A broke through (greater than 0.1 ppm) the IRA-400 resin bed after 90 bed volumes, compared to less than 20 bed volumes for the MP-500. This is quite a dramatic difference from that observed using the effluent B solution. This indicates that the resin chosen for treatment of a mill effluent solution will be site specific.

The loading isotherms are provided in Figures 1 and 2 for column I. After 140 bed volumes of effluent had passed through the Amberlite IRA-400 column, the resin was fully loaded with respect to copper and iron. However, nickel and zinc were still being removed by the resin. The loading capacities for the IRA-400 resin after 140 bed volumes were: (mg/mL resin) Cu, 23.4; Fe, 0.3; Ni, 0.6; and Zn, 15.1.

Table 5

COLUMN I EFFLUENT ANALYSIS; TEST 3
(IRA-400 AND EFFLUENT A)

Bed Volumes	Column I Effluent Analysis, ppm				
	Cu	Fe	Ni	Zn	pH
30	-	0.06	-	0.03	11.7
50	-	0.06	-	0.02	11.6
70	0.008	0.06	0.002	0.05	11.6
80	0.06	-	0.06	-	11.6
90	0.13	0.06	0.06	-	11.6
100	2.1	-	-	-	-
110	27	1.62	0.11	0.95	11.6
120	102	-	-	4.0	11.6
140	222	2.90	0.70	24	11.5
160	-	-	-	47	11.5
180	256	3.87	2.66	71	11.4
190	-	-	2.11	-	11.4
270	206	2.33	4.15	70	11.0

0656A

Table 6

COLUMN I EFFLUENT SOLUTION ANALYSIS; TEST 4
(MP-500 AND EFFLUENT A)

Bed Volumes	Column I Effluent Analysis, ppm				
	Cu	Fe	Ni	Zn	pH
10	0.08	0.07	0.07	0.01	11.2
20	1.56	0.11	0.10	1.1	11.6
30	5.54	0.19	0.16	2.1	11.6
50	69	1.45	1.60	40	11.6
80	103	1.49	2.02	42	11.6
140	241	2.18	4.12	69	11.6

0656A

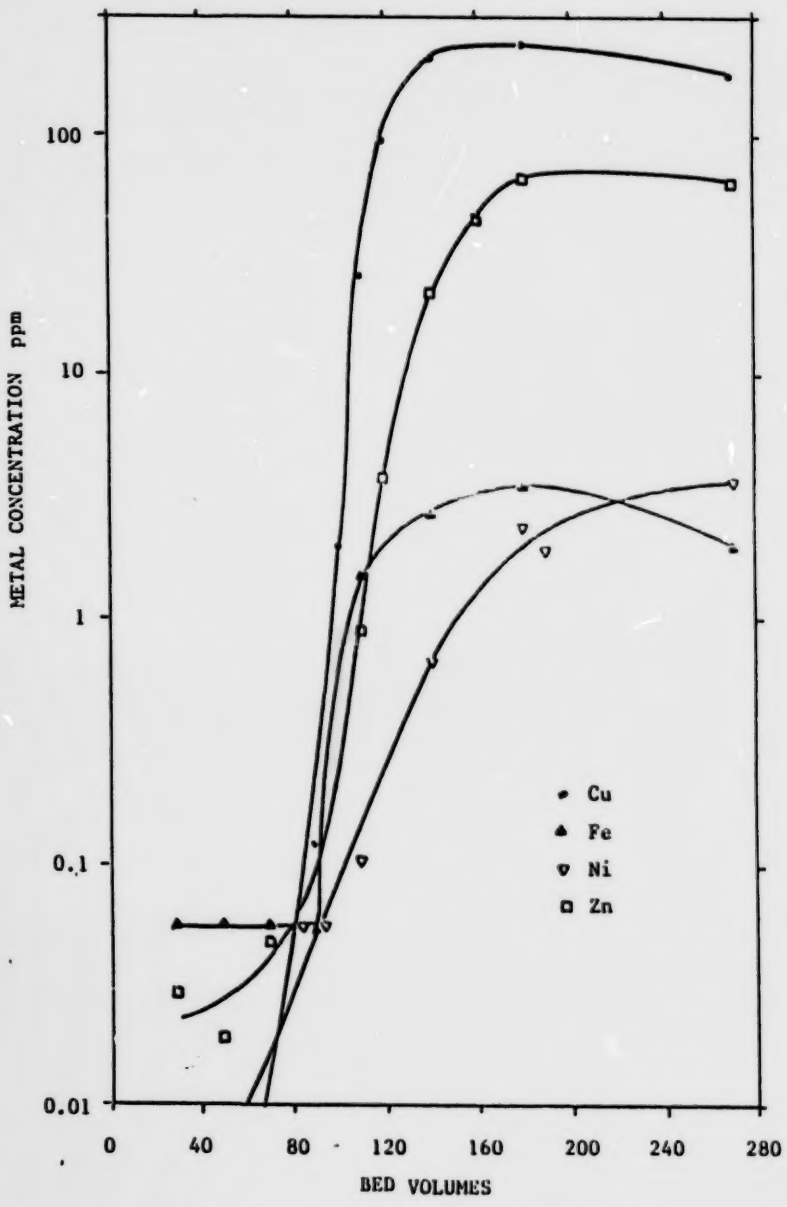


FIGURE 1 : TEST 3 COLUMN 1 LOADING ISOTHERM
(EFFLUENT A USING IRA-400 RESIN)

WD1

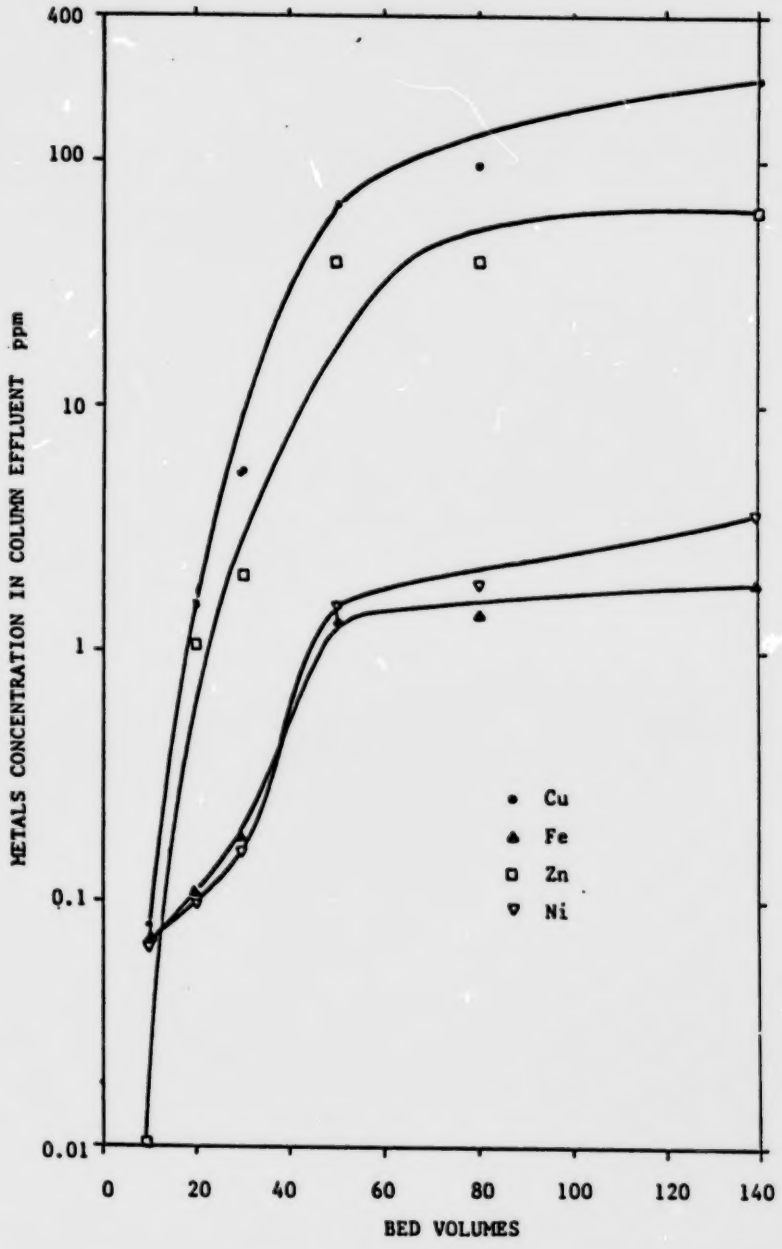


FIGURE 2: TEST 4. COLUMN 1 LOADING ISOTHERM
(EFFLUENT A USING MP-500 RESIN)

For the MP-500 resin, although copper was fully loaded after 140 bed volumes, iron, nickel and zinc were still being removed from the feed solution. The loading capacities for the MP-500 resin after 140 bed volumes were: (mg/mL resin) Cu, 13.7; Fe, 0.2; Ni, 0.3; Zn, 4.9.

The loading isotherms for the secondary columns, for the removal of free cyanide, are provided in Figures 3 and 4, for Test 3 (IRA-400) and Test 4 (MP-500) respectively.

For test 4, the macroporous resin preconditioned with cuprocyanide, displayed the same "royal barren" behaviour as described by Gilmore (12). Cyanide in the column effluent exceeded 1 mg/L after 14 bed volumes, and then dropped to 0.05 mg/L at 48 bed volumes, before breakthrough (greater than 0.1 mg/L CN) which occurred gradually after 60 bed volumes.

The gel-type resin, (Amberlite IRA-400, test 3), also showed royal barren behaviour, reaching 0.88 mg/L CN(t) after 24 bed volumes. This decreased to a minimum of 0.25 mg/L CN(t) after 48 bed volumes. The level of less than 0.1 mg/L was achieved only during the first 12 bed volumes. Again, breakthrough occurred gradually after 44 bed volumes.

For the column II operation, the two resins performed comparably. Both resins leaked cyanide to about the 1 mg/L level during the initial bed volumes; the MP-500 resin performed better at achieving the 0.1 mg/L target value after the royal barren.

More information on "royal barren" behaviour for column II is provided in Appendix III Section 3.0, which describes the results of the test program carried out on column II.

0656A

WD1

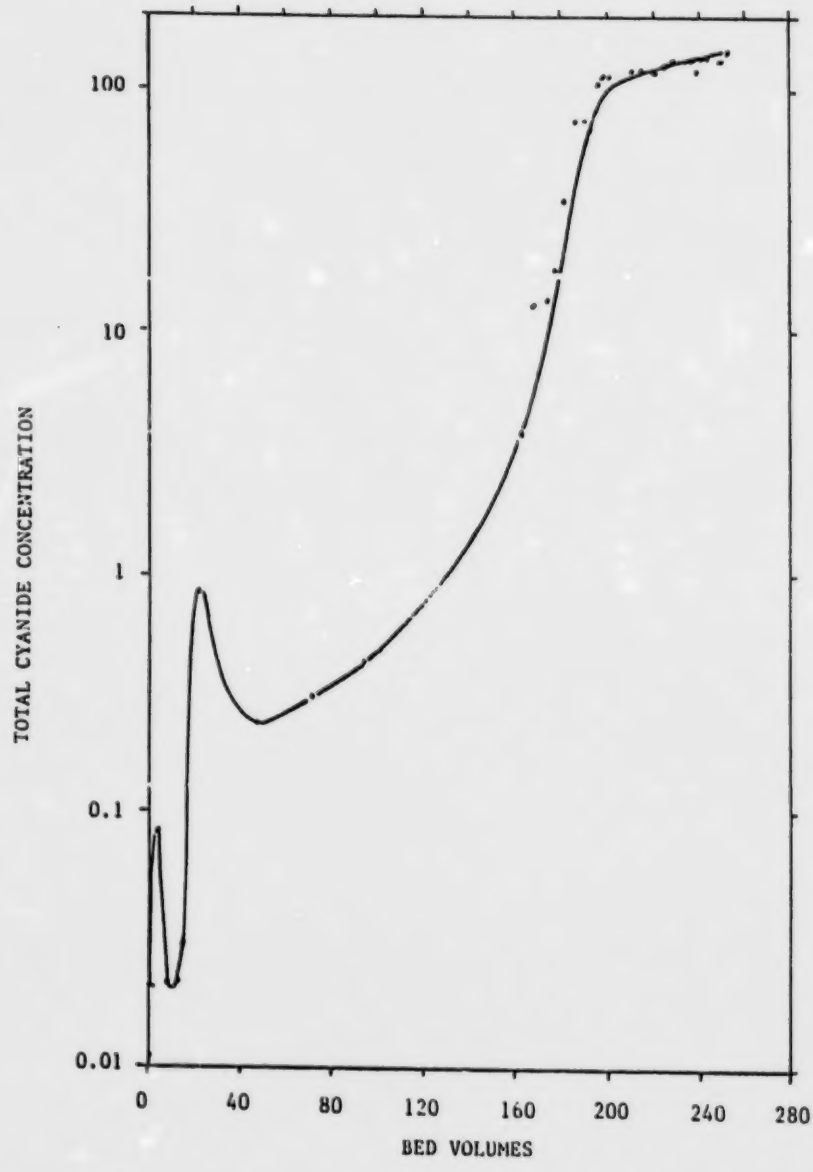


FIGURE 3: TEST 3, COLUMN 2 LOADING ISOTHERM
(EFFLUENT A USING IRA-400 RESIN)

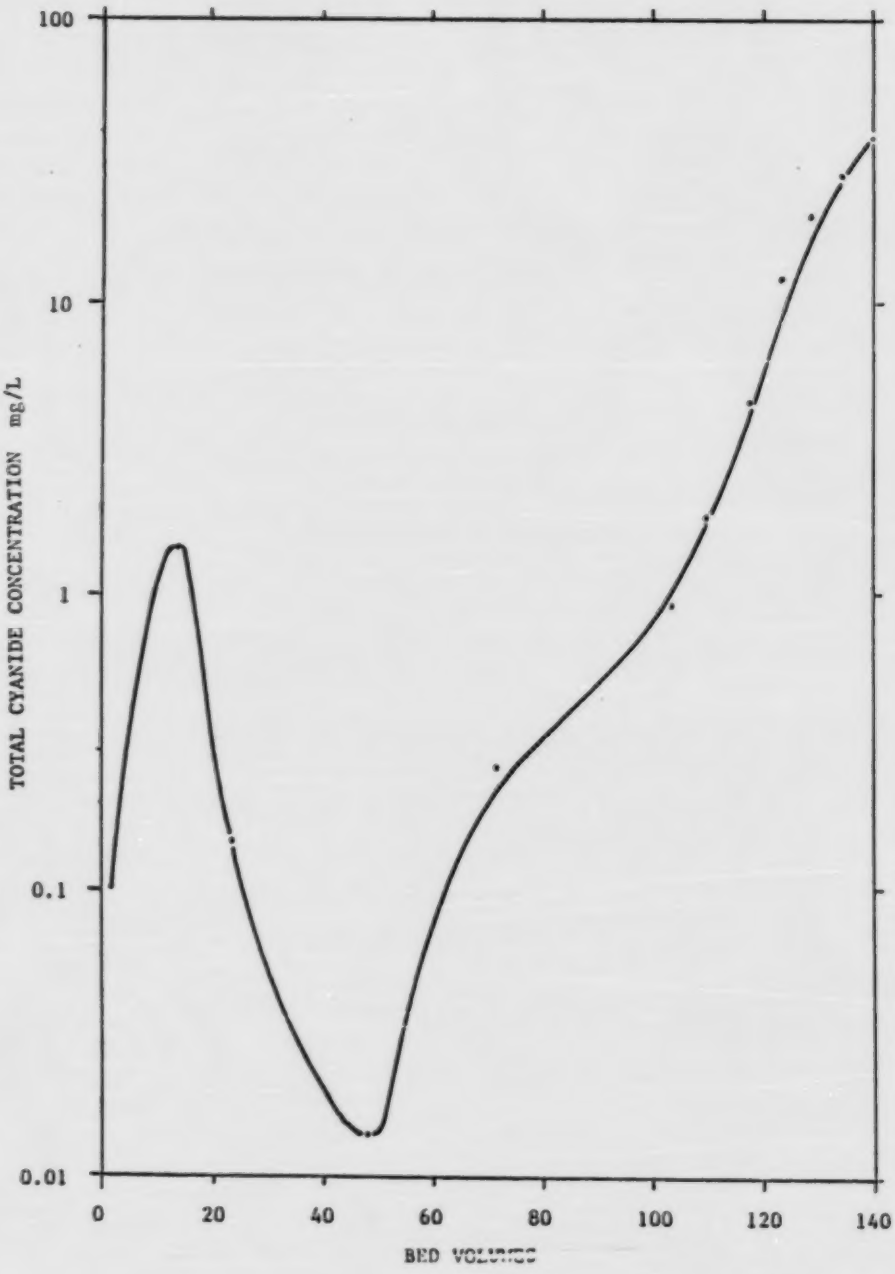


FIGURE 4 : TEST 4. COLUMN 2 LOADING ISOTHERM
(EFFLUENT A USING MP-500 RESIN)

APPENDIX III

A.III.2.0 COLUMN I TESTWORK

After the resin selection testwork described above, the two columns were tested separately. The initial testwork had provided adsorption data for column I, including barren levels, breakthrough and equilibrium capacities, as well as loading isotherms. Therefore, the further testwork carried out on column I began with an investigation into the elution operation.

Prior work conducted at Witteck had indicated that the sulphuric acid strip recommended by Gilmore (12) for desorption of the primary column would not elute copper efficiently from the resin. Therefore, a reinvestigation of the elution operation was undertaken.

A.III.2.1 Background

In the 1976 CANMET report (12) the loaded primary column was desorbed by a downflow of a 1% H_2SO_4 solution.

$$(Resin^+)_2\text{-}M(CN)_4^{2-} + 2H_2SO_4 \longrightarrow (Resin^+)_2SO_4^{2-} + MSO_4 + HCN$$

The eluate, containing metal sulphates and HCN was passed downflow through a cation exchange column for recovery of the metals.

$$2\ Resin^-H^+ + MSO_4 \longrightarrow (Resin^-)_2M^{2+} + H_2SO_4$$

The effluent from the cation exchange column, containing HCN and sulphuric acid, was collected in a 1.4 N NaOH trap. Any gaseous HCN not collected in the primary trap was recovered in a secondary caustic aspirator trap. The metals (Cu, Zn, Ni) were recovered by brine desorption of the cationic exchange resin.

WD1

The loading capacities for cyanide and the base metals on the resin apparently were calculated from the amount of each recovered in the caustic traps and brine eluate, respectively, during elution. There was no mass balance for the amount of cyanide and base metals removed from the mill effluent during loading of the anionic and cationic exchange resins, and the amounts eventually recovered during the stripping process.

The overall percent recovery of cyanide is of the utmost importance since the ability to recycle the cyanide back to the cyanidation leach circuit plays a major role in the economic viability of the whole ion exchange process.

Furthermore, in a full scale operation, the cyanide would most likely be recovered from the acidic regenerant solution in a scrubber column, where the acidic solution would pass downflow countercurrent to a stream of air. The air would displace the HCN from the regenerant solution. The air and HCN would then pass upflow through an absorber column where it would be contacted countercurrently with an alkaline absorber solution. The HCN would be removed through the air stream and trapped as CN^-. Since the cyanide would be released from the regenerant solution as HCN, the overall percent recovery is important due to safety considerations as well as economic considerations.

The overall percent recovery of the base metals would indicate which metals, if any, were not fully removed from the resin during stripping, and therefore might be acting as resin poisoning agents. This information was not obtained during the original CANMET work.

0700A

WD1

During the present work, the overall percent recovery of cyanide was investigated stepwise. First of all, the amount of cyanide present in an acidic regenerant solution, which can be released as HCN and then recovered in an alkaline trap, was determined. The results of this testwork are reported in Appendix III Section 2.2, "Recovery of HCN from Acidic Regenerant Solution".

Secondly, the stripping procedure for removal of base metals and cyanide from loaded anionic exchange resins was investigated. In addition to the 1% sulphuric acid strip which CANMET utilized, a second stripping procedure which was developed by Witteck in conjuncton with Lac Minerals in 1981, was tested. The removal of cyanide and base metals from the resin was quantified, and the concentration of reagents in the regenerant solution optimized. The results of this work are reported in Appendix III Section 2.3 "Stripping of Resin Loaded with Metal Cyanide Complexes".

Stripping isotherms were generated and are reported in Appendix III, Section 2.4.

Twenty-two loading/stripping cycles were carried out on column I, and a mass balance was maintained for Cu, Fe, Ni and Zn. The overall loss in resin capacity after 22 cycles was determined. The results of this testwork are presented in Appendix III, Section 2.5.

Potential resin poisoning agents were investigated, using "spiked" mill effluent (Sb, As, Co, Hg and Mo). These results are provided in Appendix III, Section 2.6, along with the results of testwork on selective elution procedures for their removal from the "poisoned" resin.

0700A

WD1

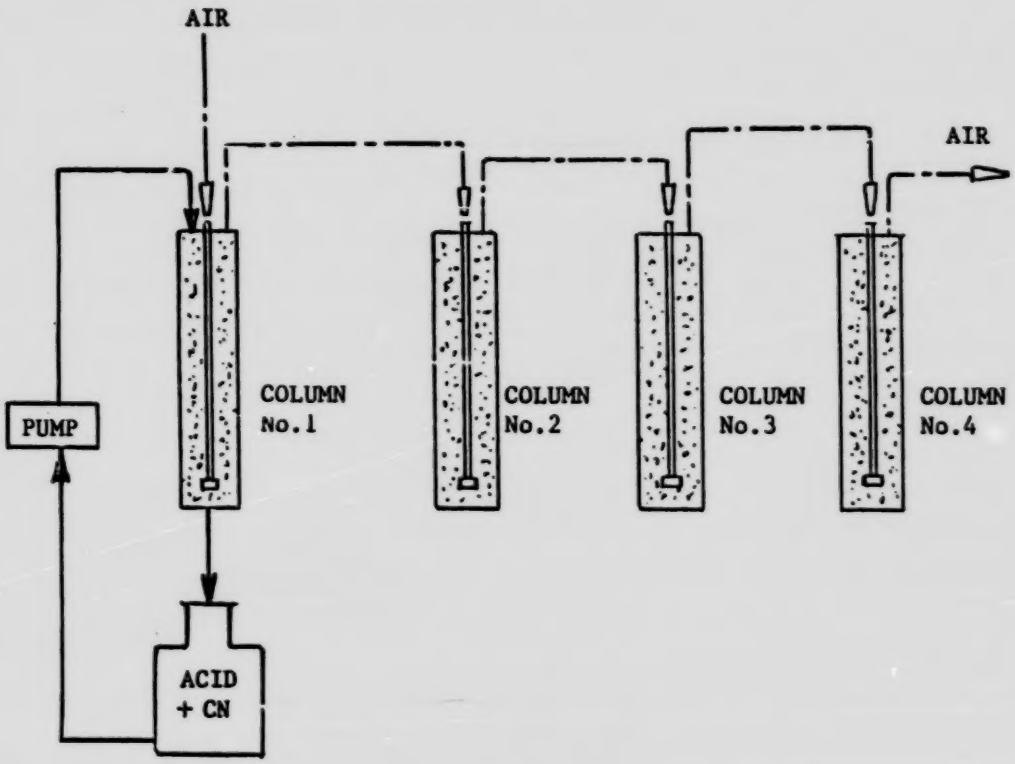
Finally, testwork was performed on an effluent from the Hemlo area in an attempt to identify a resin and the conditions required to remove antimony and arsenic from waste effluent using ion exchange resins. The results of this work are provided in Section 2.7.

A.III.2.2 Recovery of HCN from an Acidic Regenerant Solution

In order to evaluate the trapping of HCN using an alkaline trap, a series of six tests was carried out. For the initial five tests, a synthetic solution, containing sulphuric acid (pH 0.7 to 1.5) and sodium cyanide, was used to mimic the acidic regenerant solution during stripping. In two of these tests (Test 1 and 2) base metals (Cu and Zn) were added to more closely mimic the regenerant solution for the primary column, and to determine if the presence of base metals has any inhibitory effect on the release of HCN from acidic solution. For the sixth test, resin loaded with metal cyanide complexes was stripped, and the HCN recovered. A number of different solutions were tested for the alkaline trap, including sodium hydroxide, as well as mill effluent, pH adjusted with either sodium hydroxide or lime. The six tests are described below.

Test 1

The first test was carried out using the apparatus shown in Figure 13. The sulphuric acid solution (1 L), representing the spent regenerant solution which would report to a scrubber column during stripping, was prepared by dissolving 17.1 g/L CN as NaCN, 1 g/L Cu as $CuSO_4$ and 10 g/L Zn as $ZnSO_4$ in water and maintaining the pH at 1.5 using sulphuric acid. The acidic solution was recirculated (100 mL/min) through a glass column which contained glass beads to mimic the raschig rings of a scrubber column. Air was passed upflow through the scrubber column and then through three alkaline absorber columns in series. Air flow was controlled at 0.5 L/min by use of an air flowmeter. For Test 1, three alkaline traps connected in series scrubbed the HCN from the air. Each trap contained 100 mL of 1% NaOH, pH 12.9.



——— REGENERANT SOLUTION

——·—— AIR

COLUMN No.1 --- REGENERANT SOLUTION

COLUMN No.2 TO No.4 --- 0.1M NAOH

FIGURE 5 : APPARATUS USED FOR TEST 1 OF HCN RECOVERY TESTWORK

WD1

Samples were taken periodically (approximately every hour) from the regenerant solution, stabilized to pH 12 using sodium hydroxide pellets and analyzed for titratable cyanide using a standard $AgNO_3$ solution. The test was continued until the cyanide level by titration was below the detection limit (< 5 ppm). This required 46 hours. At this point, the test was terminated, and the amount of cyanide in the three alkaline traps was determined. The results are summarized below:

Trap	pH	CN mg
1	11.5	393.5
2	10.7	964.0
3	10.5	581.0
Total:		1938.5

At completion of the test, the three alkaline traps contained only 1.94 g of cyanide, representing only 11.3% recovery of cyanide. The second trap, at a final pH of 10.7, contained more cyanide than the first trap. This indicates that the cyanide was being scrubbed through each trap in sequence. The pH would drop as the HCN was absorbed, to at least as low as pH 10.5, as indicated by trap 3. At this pH, the HCN could be scrubbed slowly from trap to trap, resulting in a subsequent rise in pH back to pH 11.5, as indicated by trap 1. This situation is the result of insufficient sodium hydroxide being present in the alkaline absorbers to maintain the pH greater than 11.5. As indicated by Figure 14, cyanide is present 100% as CN^- at pH values greater than 11.5. For test 2, and all subsequent testwork in this section unless indicated, the alkaline traps were monitored for pH and maintained at pH greater than 11.5 by the addition of sodium hydroxide or lime.

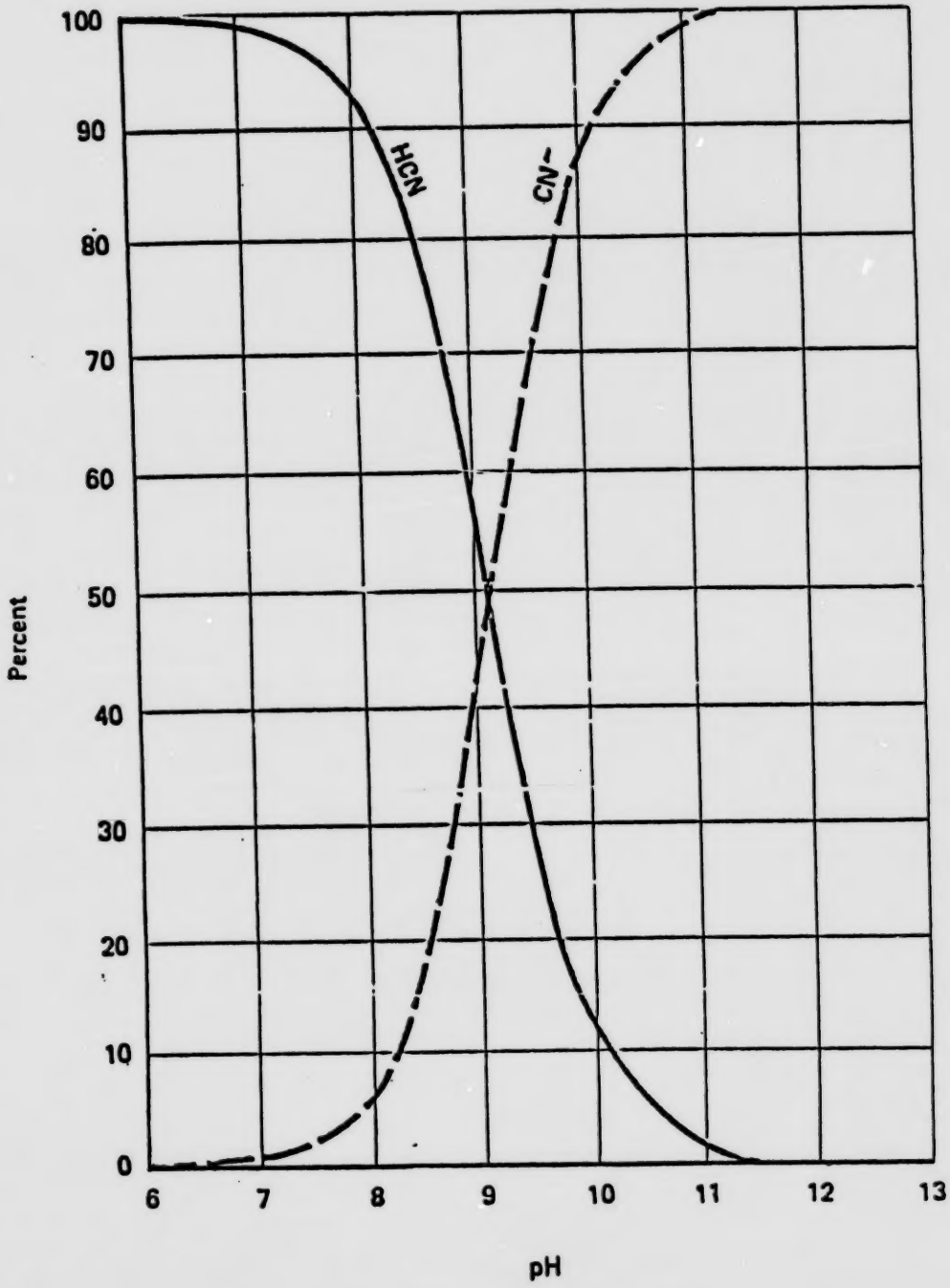


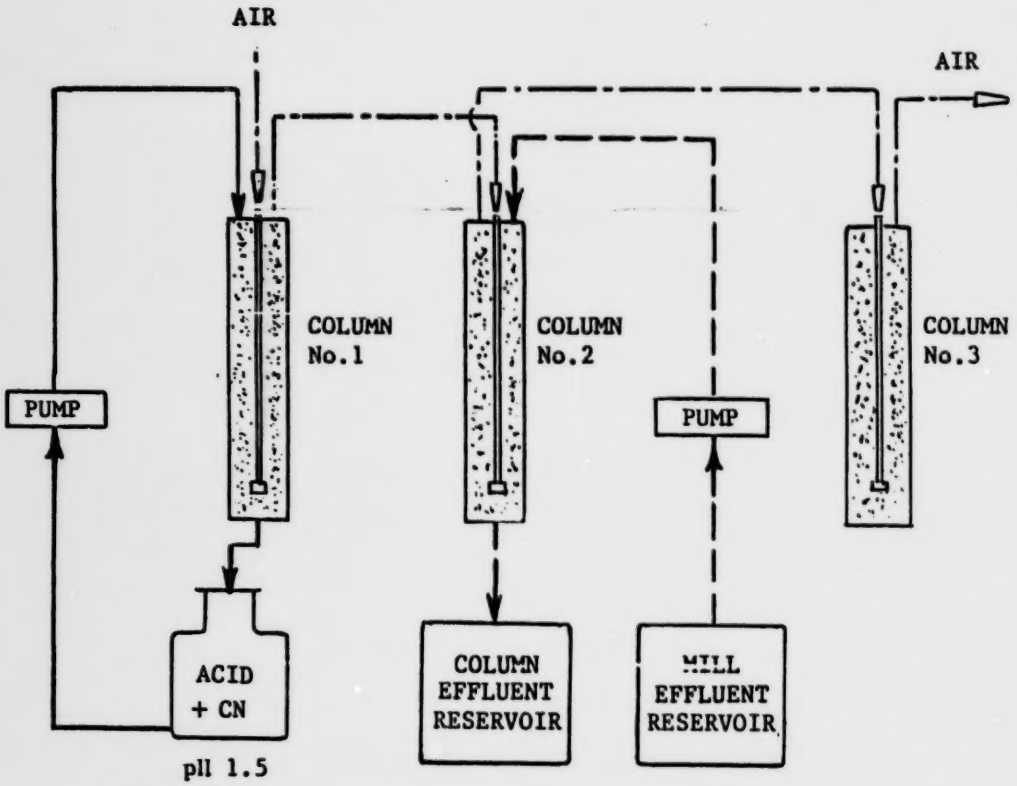
FIGURE 6 : RELATIVE AMOUNTS OF HCN AND CN AS A FUNCTION OF pH

Test 2

During this test, the synthetic regenerant solution was prepared as described for Test 1. Rather than using sodium hydroxide in fresh water for the primary trap, mill effluent was tested for its ability to absorb HCN. For the CANMET two column system, rather than using fresh water, a portion of the effluent from the first column containing only free cyanide might be used to trap the cyanide released from the first column during stripping. This cyanide-enriched solution could then be recycled to the leach circuit.

For this test, the apparatus used was similar to that described above for Test 1, except that there were only two alkaline traps (see Figure 7). Trap 2 contained 1% NaOH and was maintained at pH greater than 11.5. Mill effluent A (20 L, maintained pH 11.5 with NaOH) was pumped (50 mL/min) from a feed reservoir downflow through the second absorber column, and was collected in a second reservoir. A sample of the mill effluent was removed for cyanide analysis from the collection reservoir, and then the mill effluent was returned to the feed reservoir. In all, the 20 L of mill effluent was passed through the absorber column eight times.

The increase in the cyanide concentration in the mill effluent after each passage of 20 L was recorded. At the completion of the test, which required 42 hours, both alkaline traps were assayed for cyanide. The results are summarized in Table 7.



——— REGENERANT SOLUTION

— — — MILL EFFLUENT ALKALINE TRAP SOLUTION

——·—— AIR

COLUMN No.1 --- REGENERANT SOLUTION, GLASS BEADS AND SPARGER IN COLUMN

COLUMN No.2 --- ALKALINE TRAP - EFFLUENT A (20 L), GLASS BEADS AND SPARGER IN COLUMN

COLUMN No.3 --- CAUSTIC (SECONDARY) TRAP -0.25M NaOH (600 mL), GLASS BEADS AND SPARGER IN COLUMN

FIGURE 7: APPARATUS USED FOR TEST 2 OF HCN RECOVERY TESTWORK

WDI

Table 7

TEST 2: RECOVERY OF HCN IN ALKALINE TRAP

Passage	Mill Effluent Volume, L	Mill Effluent CN mg/L	Cumulative Cyanide Trapped g	Cumulative Cyanide Trapped %
Head	-	533	0	-
1	20.0	833	6.00	35.1
2	19.6	983	8.82	51.6
3	19.1	1083	10.50	61.4
4	18.8	1133	11.28	65.8
5	18.8	1233	13.16	77.0
6	18.1	1343	14.66	85.7
7	18.0	1343	14.58	85.3
8	17.9	1343	14.50	84.8
Second Trap (% NaOH)	0.6	-	0.081	0.5

0700A

Effluent A, originally assayed 533 mg/L CN(t) was enriched in cyanide to 1343 mg/L CN(t) by completion of Test 2.

The mill effluent trapped 86% of the cyanide (14.66 g) after the 20 L had been recirculated through the absorber column 6 times. After this, a slight loss in the percent cyanide trapped was noted, due mostly to sampling. The second trap contained less than 1% of the cyanide.

The amount of cyanide removed by sampling was taken into account, and accounted for an additional 1273 mg CN or 7.4% of the cyanide. Therefore, the cyanide reported as follows:

	CN (mg)	%
Regenerant - initially	17100	100
Mill Effluent (Trap 1)	14660	85.7
1% NaOH (Trap 2)	81	0.5
Removed by sampling	1273	7.4
TOTAL:		93.7%

A total cyanide determination was not carried out on the final regenerant solution. However, it is most likely that the 6% cyanide unaccounted for was lost from the regenerant as HCN during the sampling procedure, which involved opening the regenerant tank.

On a plant scale, greater than 94% recovery of CN could be expected, as the sampling would represent an insignificant proportion of the total cyanide present.

0700A

This test also indicated that a second trap may not be necessary if the pH of the first trap is maintained at or above pH 11.5.

Operation of the mill effluent trap was complicated by the formation of a precipitate in the reservoir which coated the walls of the column and the glass beads. The precipitate was most likely $CaCO_3$ formed by absorption of CO_2 into the alkaline solution. During a subsequent test these solids were collected and assayed (see Test 3).

Tests 3, 4, 5

Three tests were carried out under similar conditions to those described above. However, the pH of the mill effluent trap was adjusted using lime instead of NaOH, since lime is a less expensive reagent. For test 3, it was noted that copious amounts of lime were required to maintain the pH at 12. Unfortunately, the amount of lime added was not recorded. As pH 12 is the maximum that lime can acheive, tests 4 and 5 were identical except that the pH was maintained at 11.5 and 11.0, respectively, to determine if greater than 90% of the cyanide could be recovered while maintaining a slightly lower pH, thereby reducing the lime consumption. For tests 4 and 5, the lime requirement was recorded.

To test whether the lime/effluent trap was efficient, a caustic/ effluent trap was added to the circuit as a second absorber trap. The 1% NaOH trap remained as a third trap. The apparatus used in tests 3 to 5 is shown in Figure 8.

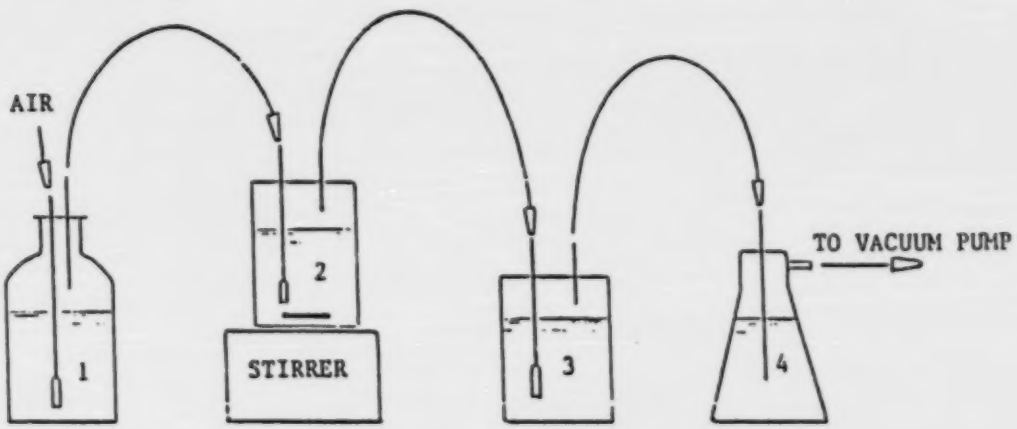
0700A

Table 8

TESTS 3, 4, 5: RECOVERY OF HCN IN ALKALINE TRAPS

	Regenerant				Cyanide Recovered							
	CN added	CN remain			Trap 1		Trap 2		Trap 3		CN Total	
Test	mg	mg	%	pH	mg	%	mg	%	mg	%	mg	%
3	9960	690	7	12.1	7515	75	14	0.1	-	-	8219	83
4	4980	95	2	11.5	4291	86	183	3.7	3	0.1	4572	92
5	4990	155	3	11.0	3931	79	280	5.6	6	0.1	4372	88

For Test 3, conducted with trap 1 at pH 12, there was negligible cyanide present in traps 2 or 3. Seventy-five percent of the cyanide was recovered in trap 1. For Tests 4 and 5, where trap 1 was maintained at pH 11.5 and 11.0, respectively, there were progressively higher levels of cyanide reporting to the second trap. In all cases, the third trap contained little or no cyanide and therefore was not required. For tests 4 and 5, the lime requirements to maintain the pH of the primary trap at pH 11.5 and 11.0, respectively, were 17.2 and 13.7 g of lime, respectively, whereas the percentage of cyanide "escaping" from trap 1 increased from 3.7% to 5.6%. The savings due to reduced lime consumption would have to be weighed against the capital and operating costs of a caustic scavenger trap for cyanide.



1. ACID / CN SOLUTION (1 L)
2. EFFLUENT / LIME TRAP (0.8 L)
3. EFFLUENT / CAUSTIC TRAP (0.8 L)
4. NaOH SOLUTION (0.2 L)

FIGURE 8: APPARATUS USED FOR HCN RECOVERY TEST 3,4,5

In addition, work was being carried out concurrently on cyclic adsorption/elution of the primary column (see Appendix III, Section 2.5). This work indicated that, at least on laboratory scale, sparging air through the regenerant and alkaline tanks was more effective for cyanide removal and recovery than using scrubber and absorber columns. Since this operation is simpler, sealed 2 L containers were used with air spargers, rather than columns with glass beads as described above for tests 1 and 2.

For test 3, the synthetic regenerant contained 10 g of CN as NaCN dissolved in 1 L of sulphuric (pH 0.7). For tests 4 and 5, base metals were not added and the cyanide concentrations were reduced to 5 g/L. Rather than sampling the regenerant solutions, the tests were terminated when the alkaline traps reached maximum cyanide concentration.

The data for the recovery of cyanide in the primary trap is provided in Figure 9 , for tests 3, 4 and 5. The data presented has been corrected for the amount of cyanide removed from trap 1 with each sample. It can be seen that test 3 was terminated prematurely, 7% of the cyanide remained in the acidic regenerant solution. Tests 4 and 5 were complete within 6 h, a substantial improvement over tests 1 and 2, although there was less cyanide present. The percent cyanide recovery for the three traps, as well as that remaining in the regenerant solution at shutdown, is provided in Table 8. The amount of cyanide listed for each vessel includes the amount removed from each vessel due to sampling.

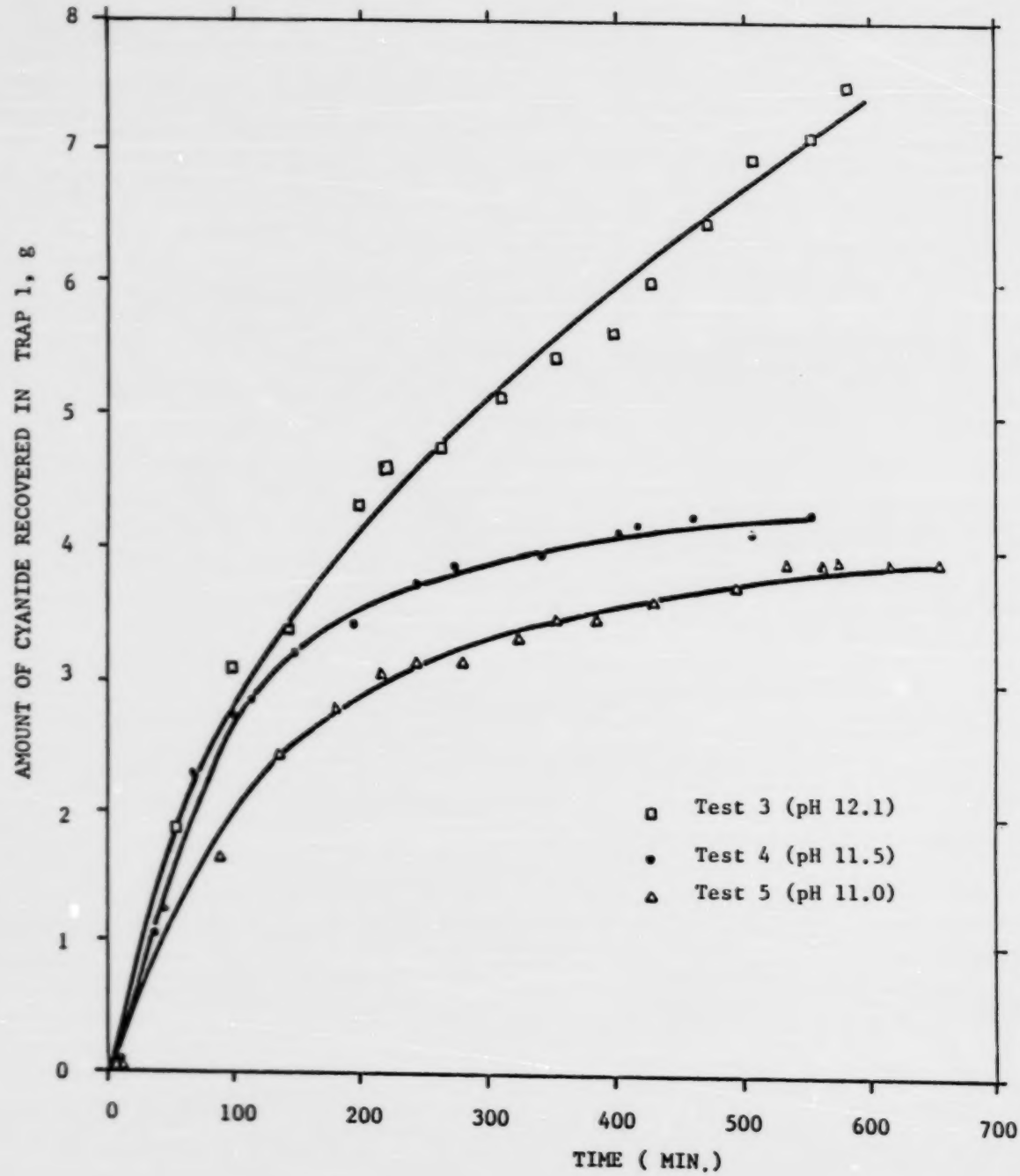


FIGURE 9 : RECOVERY OF HCN IN ALKALINE TRAPS (TEST 3,4,5)

For tests 3 and 4, 90 and 85% of the cyanide, respectively, reported to the alkaline traps. The overall recovery of cyanide, including that remaining in the acidic regenerant, was 83, 92 and 88% for tests 3, 4 and 5, respectively.

As shown by test 3, a mill effluent trap can be enriched in cyanide by at least 10 g/L. During all three tests, solids formed in the mill effluent solutions. For test 3, these solids were collected (12.6 g from trap 1) and assayed: 30.0% Ca; 0.13% CN(t); 0.034% Fe; 0.016% Zn. Therefore, these solids are $CaCO_3$, which forms due to the absorption of CO_2 by the alkaline solution. Calcium carbonate is 27.7% Ca, and is soluble to only 15 mg/L.

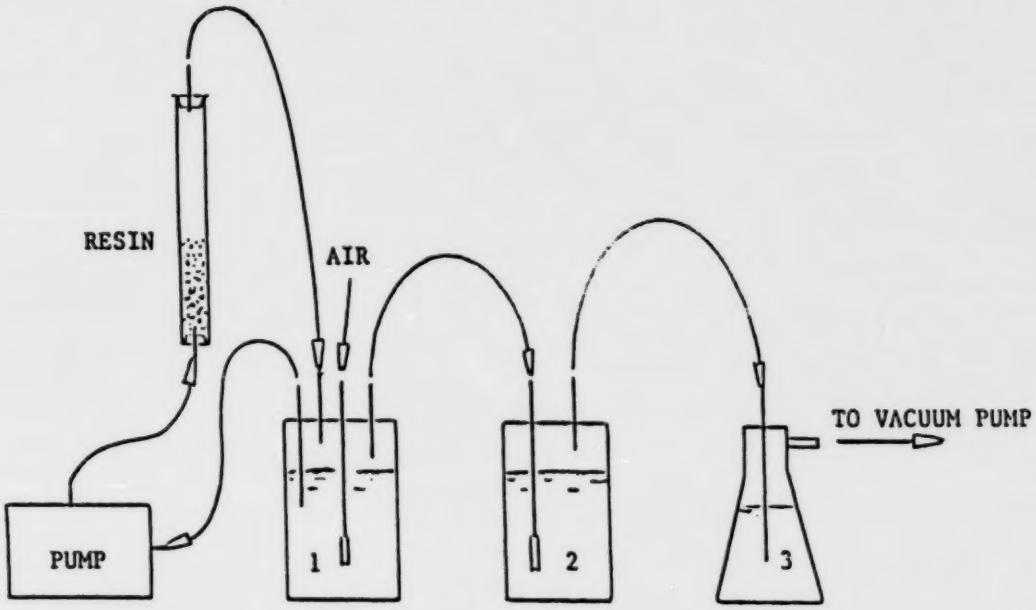
Test 6

For test 6, a 20 mL (9.24 g) sample of Lewatit MP-500 resin, which had been batch-loaded using effluent A, was stripped using the apparatus shown in Figure 10.

The regenerant solution (0.1 M H_2SO_4; 800 mL) was recirculated upflow through the resin bed. Air was sparged through the regenerant solution, and then through two alkaline traps connected in series. Trap 1 contained 800 mL of effluent A maintained at pH 11.5 using lime. Trap 2 contained 400 mL of sodium hydroxide solution, maintained at pH greater than 12.

Analysis of the resin prior to stripping is provided below:

	CN(t)	Zn	Cu	Ni	Fe
Resin Analysis %	13	7.9	6.2	0.16	0.3



1. REGENERANT
2. EFFLUENT / LIME
3. NaOH SOLUTION

FIGURE 10: APPARATUS USED FOR HCN RECOVERY TEST 6

Since 9.24 g of resin were used, 1.2 g of cyanide were present in the system. Stripping was carried out for 6 hours, at which time the concentration of cyanide in trap 1 had reached a maximum, and had started to decrease. The pH of the effluent in trap 1 had been maintained in excess of pH 11.5 throughout the test. However, when the test was completed, and the agitation caused by the air flow was ceased, the supernatant had a pH of only 10.0. The amount of cyanide recovered in trap 1 with respect to time is presented in Figure 11. After 3 hours, 81% of the cyanide was contained in trap 1. At completion of the test, 58% of the cyanide was present in trap 1. The second trap was assayed for cyanide, and accounted for a futher 34% (1010 mg/L; 0.4 L). Therefore, 92% of the cyanide was recovered in the alkaline traps, based on the cyanide loading of the resin.

Extrapolation of the curve for trap 1 (see Figure 11) indicated that the 1.2 g of cyanide present would have required about 6 hours to report to trap 1. This is in agreement with the 92% recovered which was observed in the combination of traps 1 and 2 after 6 hours.

In conclusion, a summary of tests 2 to 6 is provided in Table 9.

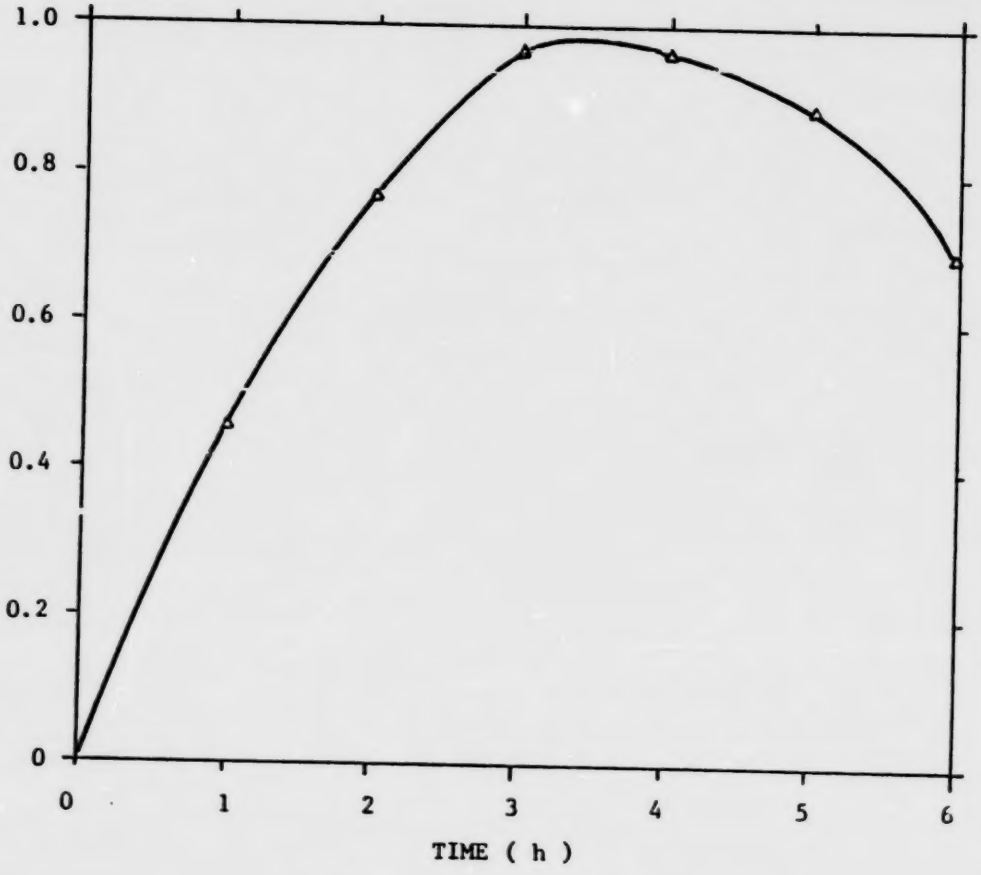


FIGURE 11: TEST 6. AMOUNT OF CYANIDE RECOVERED IN TRAP 1 VERSUS TIME

Table 9

SUMMARY OF TESTWORK ON THE RECOVERY OF HCN IN ALKALINE ABSORBERS

Test	Cyanide Present g	Metals Present	Absorber Solution	Cyanide* recovered in Traps %	Time Required hours
2	17.1	yes	Effluent & NaOH	94	42
3	9.96	no	Effluent & Lime	75	na
4	4.98	no	Effluent & Lime	90	6
5	4.99	no	Effluent & Lime	85	6
6	1.20	yes	Effluent & Lime	92	6

* Includes cyanide present in samples

It is believed that the excessive amount of time required for Test 2 was due to the apparatus. In this test, the acidic regenerant solution was recirculated through a scrubber column. The bulk of the solution at any one time was present in the holding tank, where it was not in contact with air. In tests 3 to 6, the regenerant tank was sparged continuously with air, thereby improving the efficiency of cyanide recovery.

From the data presented in Table 9 for tests 4, 5 and 6, it appears that neither the amount of cyanide present, nor the presence of base metals has a significant impact on the time required to remove HCN from an acid solution.

For tests 2, 4 and 6, greater than 90% of the cyanide present was recovered in the alkaline traps. Test 3 was not carried out to completion. It is believed that greater than 90% recovery could be expected in a full scale situation.

A.III.2.3 Elution of Resin Loaded with Metal Cyanide Complexes

Prior to carrying out adsorption/elution cyclic testwork, six elution tests were carried out on resin loaded with metal cyanide complexes, in order to optimize the elution procedure and to ensure high percent recoveries of base metals and cyanide from the resin.

The regenerant solution used by CANMET for column I was a 1% sulphuric acid (0.1 M) solution. Prior work at Witteck had shown that acid alone does not remove copper efficiently. Witteck Development Inc., in collaboration with Lac Minerals Inc., carried out testwork in 1981, to optimize the removal of copper from resins loaded with metal cyanide complexes. The testwork led to the filing of a joint provisional patent which covered the use of a new regenerant solution, which consisted of an acidic solution containing a second reagent which will be referred to as the WDI/Lac reagent. In the initial testwork on the stripping of loaded resins, the CANMET and Witteck/Lac processes were compared for the removal of base metals and cyanide from the resins.

The resin used for this testwork was Lewatit MP-500, which had been loaded previously using effluent A. Analyses of the loaded resin prior to stripping is provided in Table 10.

The resin (20 to 25 mL) was placed in a 2 cm diameter column. The apparatus used for tests 1, 2 and 3 is described in Figure 12, except that for test 1, there were no spargers in the regenerant nor the alkaline tanks, and the regenerant tank was not sealed. It was assumed at this time that sufficient solution/air contact would take place in the countercurrent columns to strip the eluate of HCN before it returned to the regenerant tank.

Table 10

OPTIMIZATION OF STRIPPING PROCESS

Test	Regenerant Acid M	Regenerant WDI/Lac g/L	Resin Analyses, Percent — Loaded Cu	Fe	Ni	Zn	Sb	CN(t)	Stripped Cu	Fe	Ni	Zn	CN(t)	% Removed Cu	Fe	Ni	Zn	CN(t)
3	0.5	None	6.19	0.0134	0.16	7.9	0.0005	13.06	5.2	0.014	0.03	0.08	n.a.	16.0	0	81.2	99.0	n.a.
5	0.5	Lowest	6.19	0.0134	0.16	7.9	0.0005	13.06	0.06	0.017	0.0069	0.0016	0.45	99.0	0	95.7	100	96.6
2	0.5	↓	6.43	0.0106	0.18	8.0	0.0005	15.00	0.037	0.0137	0.013	0.0023	0.029	99.4	0	92.8	100	99.8
4	0.5	↓	6.19	0.0134	0.16	7.9	0.0005	13.06	0.042	0.0088	0.012	0.0014	0.13	99.3	34	92.5	100	99.0
1	0.5	Highest	6.43	0.0106	0.18	8.0	0.0005	15.00	0.032	0.0094	0.058	0.0018	0.15	99.5	11	67.8	100	99.0
6	0.1	Lowest	19	0.0134	0.16	7.9	0.0005	3.06	0.060	0.022	0.011	0.024	0.025	99.0	0	99.3	100	99.8

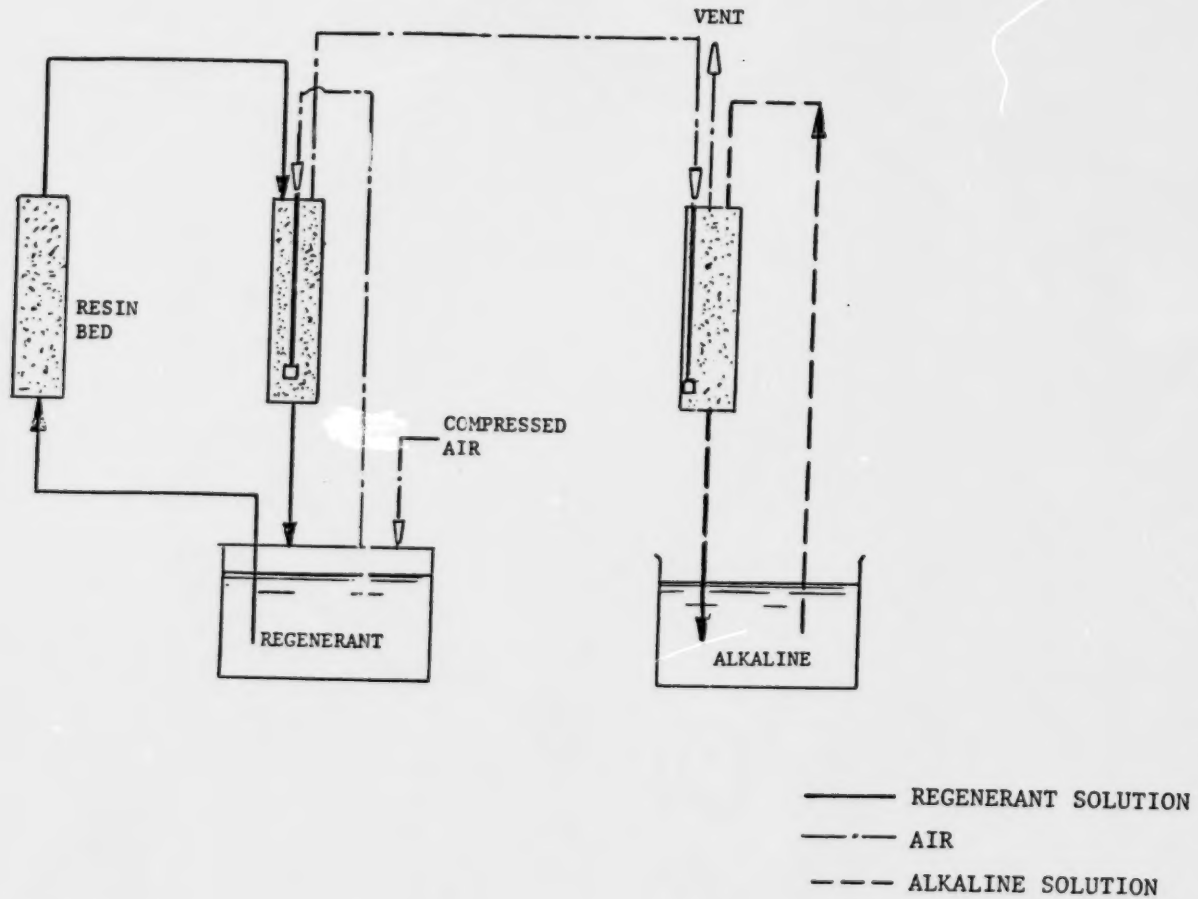


FIGURE 12: APPARATUS USED FOR STRIPPING TESTS 1 TO 3

The data for the six tests are provided in Table 10. The tests are arranged in order of increasing concentrations of the WDI/Lac reagent, except for test 6, for which the acidity was decreased five-fold and the lowest concentration of the WDI/Lac reagent was used.

For test 1, only 2% of the cyanide was recovered in the alkaline trap, although only 1% of the cyanide remained on the resin. It was concluded that most of the cyanide was being released from the regenerant tank, rather than being scrubbed from solution in the scrubber column. For tests 2 and 3, the regenerant and alkaline tanks were sealed, and air was drawn through a sparger in the regenerant tank and then through a sparger in the alkaline cyanide trap. For tests 4, 5, and 6, the scrubber absorber columns were removed from the apparatus, since better scrubbing/absorbing action occurred in the tanks rather than in the two columns.

Test 3, which used a straight 1% sulphuric acid strip, eluted only 16% of the copper from the resin. WDI/Lac reagent at the lowest concentration removed 99% of the copper and 97% of the cyanide. At greater concentrations of WDI/Lac reagent, or lower acidity, greater than 99% of both the copper and cyanide was eluted from the resin. Removal of zinc was 99% or better for all of the tests.

Although the removal of nickel was inconclusive with respect to the CANMET stripping procedure, since both test 3 (CANMET strip; no WDI/Lac reagent) and test 1 (highest concentration of WDI/Lac reagent) showed poorer nickel recovery than the other tests, the results of tests 2, 4, 5 and 6 do imply that nickel can be removed by greater than 92% using the WDI/Lac stripping procedure.

Iron loadings were very low ($\sim$ 0.0001 g Fe/g resin). The behaviour of iron is shown more clearly during the cyclic loading/stripping testwork reported in Section 2.5 of Appendix III.

The eluant used for test 6, (0.1 M acid and the lowest concentration of WDI/Lac reagent) was considered to be the optimal eluant tested, showing 99% recovery or better for Cu, Ni, Zn and CN(t), while using the lowest concentrations of acid and the WDI/Lac reagent.

A.III.2.4 Elution Isotherms

The purpose of this testwork was to produce elution isotherms to compare the CANMET stripping procedure to the Witteck/Lac process. The percent recovery of base metals (Cu, Zn) and cyanide in the acidic regenerant solution was determined.

For this testwork, 50 mL of resin previously loaded using effluent A was placed in a 2 cm diameter column. The regenerant solution was passed downflow through the resin bed at a flowrate of 0.1 bed volumes per minute. Column eluate was collected in 100 mL samples, and assayed for Cu, Zn and CN(t). In addition, the eluate was titrated for HCN and H_2SO_4 using a standard solution of sodium hydroxide (0.4 N) and using methyl orange for the first end point (sulphuric acid) and phenolphthalein for the second end point (HCN).

The stripping isotherms are provided in Figures 13 and 14, showing the amount of cyanide in the eluate determined both by titration as HCN, and by total cyanide analysis.

For Test 1, the resin was fully desorbed after 60 bed volumes using 0.1 M H_2SO_4. At this point, the cyanide level in the eluate was 0.033 g/L CN(t). For Test 2, the resin was desorbed using 0.1 M acid and the lowest concentration of WDI/Lac reagent. After 60 bed volumes the cyanide level in the eluate was 0.001 g/L CN(t).

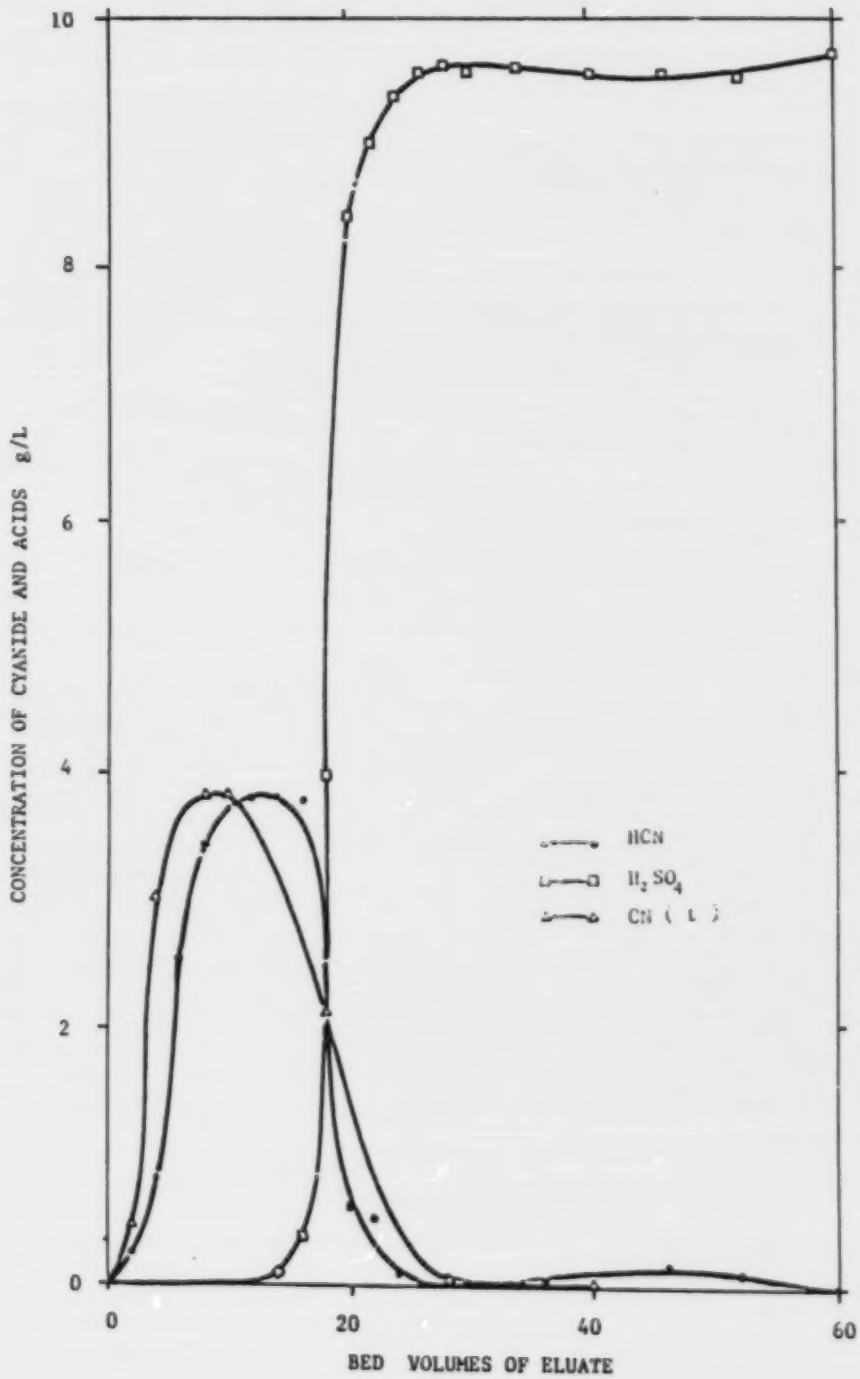


FIGURE 13: STRIPPING ISOTHERM FOR TEST 1 USING 1% SULPHURIC ACID

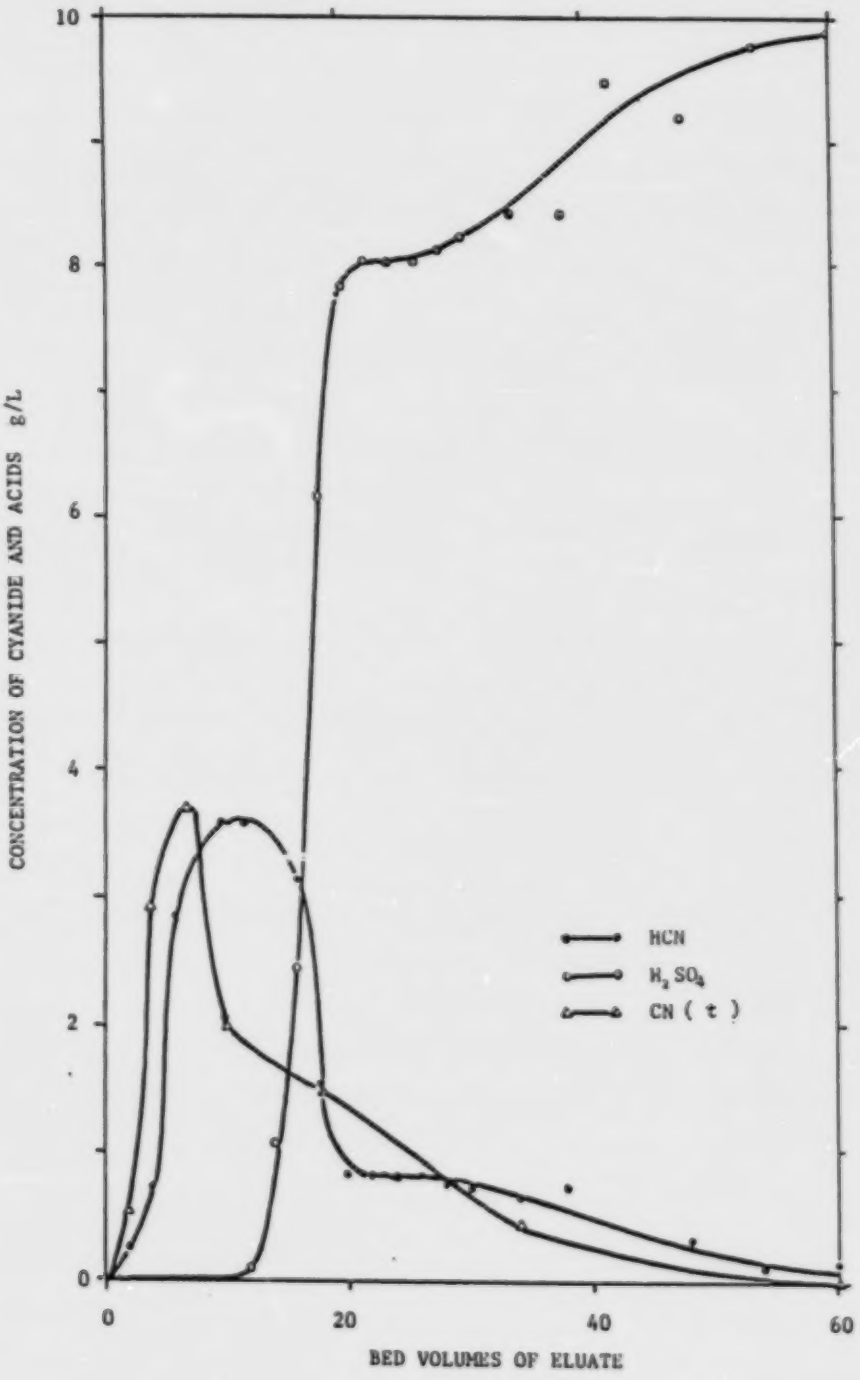


FIGURE 14: STRIPPING ISOTHERM FOR TEST 2 USING THE WDI/LAC ELUANT

The stripping isotherms for Cu and Zn are shown in Figure 15.

Although the zinc was desorbed efficiently using either procedure, the WDI/Lac reagent clearly improved the desorption of copper. The amount of CN(t), Cu and Zn present on the 50 mL sample of loaded resin, and the amount recovered using each stripping procedure is provided in Table 11.

Table 11

COMPARISON OF CANMET AND WITTECK/LAC ELUANTS FOR RECOVERY OF CYANIDE AND BASE METALS FROM RESIN

Sample	Amount g (% removed) CN(t)		Cu		Zn	
Loaded Resin (50 mL)	3.12		1.87		1.79	
Column I - Canmet Strip	3.06	(98%)	0.13	(7%)	1.53	(85%)
Column II - WDI/Lac Strip	2.88	(92%)	1.78	(95%)	1.79	(100%)

A.III.2.5 Cyclic Adsorption/Elution Testwork

Cyclic testwork was carried out on column I of the two column process, in order to observe any decrease in capacity due to the build up of resin poisoning agents. The apparatus used is that described by Figure 10. The resin (25 mL of Lewatit MP-500) was successively loaded and eluted 21 times. A composite sample of the feed solution was assayed, as well as a composite sample of the column effluent during each adsorption cycle. In this manner, the total amount of each metal loaded on the column during each cycle was determined.

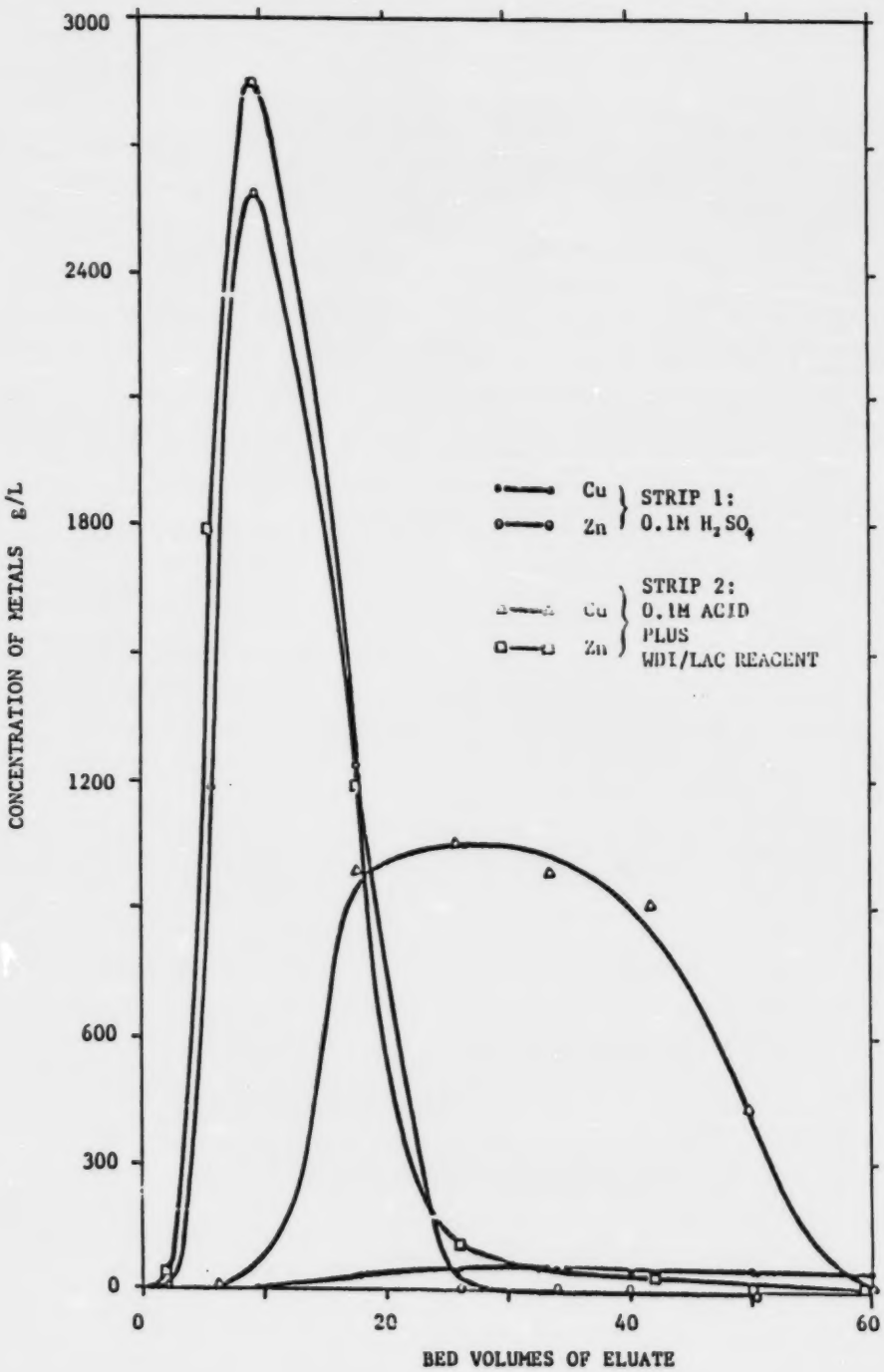


FIGURE 15: STRIPPING ISOTHERMS FOR COPPER AND ZINC

The effluent used for this testwork was effluent A. Although the composite of the feed effluent varied somewhat from cycle to cycle, typical assay of the head solution was:

Analysis, mg/L

Cu	Zn	Ni	Fe	CN	SCN	Pb	As	Sb	Hg	Co
214	140	5.4	0.06-3.4	500	150	<0.02	<0.08	<0.05	<0.02	<0.004

The amount of effluent treated during each loading cycle varied. For the first cycle, resin which had been loaded previously to full equilibrium capacity was assayed and used for the first elution cycle. After this, in order to reduce the time required per cycle, standard volumes of feed effluent were passed through the column during each adsorption cycle. At first 4 L of effluent was passed through the resin bed during each loading cycle. This was then reduced to 3, 2, and finally 1.5 L to approximate loading to breakthrough capacity. Finally, to observe any overall drop in capacity after twenty cycles, the volume of effluent was increased back to 4 L per loading cycle for comparison with the initial cycles.

To strip, the Witteck/Lac process was used. Initially, elution was carried out at the optimal conditions reported in Appendix III Section 2.3 (0.1 M acid, low concentration of WDI/Lac reagent, 1 litre). However, the concentrations were varied during the cyclic work, in an attempt to ascertain if still lower concentrations of reagents could be used. The regenerant solution was recirculated through the resin bed for 7 hours. Samples were taken at one hour intervals.

A vacuum pump was used (10 L/min) to sparge air through the regenerant solution, and then through one or two alkaline traps. The first trap contained 1 litre of sodium hydroxide solution maintained at pH 12. For cycles 14 to 21, a second trap (200 mL pH 12) was added to check for leakage of HCN from the primary trap.

0700A

WDI

After each loading/stripping cycle, the amount of base metals removed from the waste effluent by the ion exchange column during adsorption, and then recovered in the regenerant solution during elution was determined. These results for Cu, Zn, Ni and Fe are presented in Tables 12 to 15. The volume of waste effluent treated, and the concentration of the regenerant solution used for each cycle is provided in Table 16. The concentration of the WDI/Lac reagent is expressed as a factor of the "optimal" concentration determined during the preliminary stripping testwork (see Appendix III, Section 2.3).

Copper

The copper data is presented in Table 12. The far right-hand column shows the cumulative percent amount of copper remaining on the resin after each loading/stripping cycle. With the exception of the first cycle, where low copper recoveries were obtained (80%), the amount of copper remaining on the resin fluctuates at approximately 10% of the cumulative copper adsorbed. This would imply that on the average only 90% of the cumulative copper was removed per cycle. If this were in fact the case, the resin would be poisoned with copper after only 10 cycles, which was not observed. Since there is approximately a 5% error associated with each assay performed, and since any analytical error occurring early in the cyclic testwork would be carried throughout the testwork, it is assumed that there was no significant build-up of copper on the resin.

As shown in Table 16, the eluant used for cycles 1 to 4 was the best eluant tested during the preliminary stripping testwork (see Appendix III, Section 2.3). For cycles 11 to 22, the acidity was increased to 0.2 M. For cycles 9 to 20 the amount of WDI/Lac reagent was decreased to 0.7 of the optimal concentration.

Table 12

COPPER RECOVERIES DURING CYCLIC TESTWORK, COLUMN I

Cycle	Copper Loaded mg	Copper Recovered mg	Cumulative Copper Loaded mg	Cumulative Copper Recovered mg	Cumulative Copper % Remaining on Resin
1	934	737	934	737	21.0
2	668	623	1602	1360	15.1
3	684	680	2286	2040	10.8
4	720	576	3006	2616	13.0
5	588	225	3594	2841	21.0
6	505	714	4099	3555	13.3
7	572	407	4671	3962	15.2
8	576	684	5247	4646	11.5
9	537	455	5784	5101	11.8
10	402	367	6186	5468	11.6
11	382	387	6568	5855	10.9
12	388	395	6956	6250	10.1
13	398	395	7354	6645	9.6
14	285	113	7638	6758	11.5
15	291	212	7929	6970	12.1
16	292	372	8221	7342	10.7
17	372	383	8593	7725	10.1
18	299	238	8892	7963	10.4
19	389	265	9281	8228	11.3
20	336	289	9617	8517	11.4
21	320	240	9937	8757	11.9
22*	428	289	10365	9046	12.7

* After cycle 21, the resin was stripped according to the Mintek procedure (18), see text.

0700A

These variations had no discernible effect on the amount of copper stripped from the resin. However, for cycle 5, the acidity was decreased to 0.03 M acid and the WDI/Lac reagent was decreased to 0.3 times the optimal concentration. In this case, only 38% of the copper loaded during that cycle was recovered. The concentrations of both reagents were increased in cycles 6 to 8. The results for these 4 cycles (cycles 5 to 8) are tabulated below.

Cycle	Acid M	WDI/Lac g/L	Cu Recovered % *
5	0.03	0.3	38
6	0.10	0.6	141
7	0.10	0.3	71
8	0.10	0.4	119

* Refers to percentage of copper which was loaded during that cycle only.

Increasing the acidity from 0.03 M to 0.1 M but maintaining the WDI/Lac reagent at 0.3 times the optimal level increased the percent recovery from 38 to 71%. Increasing the WDI/Lac reagent still further to 0.4 or 0.6 times the optimal concentration stripped all of the copper loaded during that cycle, plus some copper which was not removed during the previous stripping cycle. Therefore, 0.1 M acid is still best, but half of the "optimal" concentration of the WDI/Lac reagent was sufficient.

For cycles 14, 15 and 16, the regenerant solution from cycle 13 was reused rather than starting with fresh regenerant each time. After each cycle, the regenerant was replenished with acid and WDI/Lac reagent to maintain the concentrations specified. This was carried out to determine at what concentration the build-up of metals in the regenerant would begin to have a detrimental effect on the stripping of metal cyanide complexes from the resin. After 3 hours of stripping during cycle 16, the regenerant solution was replaced with fresh regenerant, and the stripping for cycle 16 was continued for a further 4 hours. Copper concentrations in the regenerant solution increased from 395 mg/L for cycle 13 to 508 mg/L for cycle 14 and 720 mg/L for cycle 15.

0700A

The percent copper recovery for these individual cycles were 99%, 40% and 73% recovery, respectively. When fresh regenerant was used for stripping during cycle 16, the total percent Cu recovered increased to 127%.

Zinc

As shown in the far right-hand column of Table 13, the cumulative percent zinc remaining on the column after each stripping cycle fluctuated around 0%. The variance in acidity and WDI/Lac reagent had no effect on the amount of zinc recovered. After 21 cycles, 100% of the zinc loaded had been recovered, within experimental error. However, for cycles 14 and 15, when the regenerant solution from cycle 13 was reused, the percent recovery for the individual cycles dropped significantly; only 12% of the zinc loaded during cycle 15 was recovered during the stripping process.

For cycles 10 to 13, more zinc was recovered than was loaded during each cycle, even though there had been no build-up of zinc on the resin. The feed solution did vary somewhat when new pails of effluent A were used. Since the same feed solution was used for these four loading cycles, it is assumed that the head assay was in error. Unfortunately, insufficient sample remained to check this assay.

Nickel

The results of the cumulative percent nickel loading/stripping data is presented in Table 14. No significant build-up of nickel was observed, as indicated by the cumulative percent nickel remaining on the column.

Table 13

ZINC RECOVERIES DURING CYCLIC TESTWORK, COLUMN I

Cycle	Zinc Loaded mg	Zinc Recovered mg	Cumulative Zinc Loaded mg	Cumulative Zinc Recovered mg	% Remaining on Resin
1	894	706	894	706	21.0
2	524	600	1418	1306	7.9
3	592	620	2010	1926	4.2
4	368	391	2378	2317	2.6
5	423	378	2801	2695	3.7
6	370	341	3171	3036	4.3
7	524	531	3695	3567	3.5
8	452	594	4147	4161	-0.3
9	480	400	4627	4561	1.4
10	186	310	4813	4871	-1.2
11	220	320	5033	5191	-3.1
12	232	319	5265	5510	-4.6
13	238	310	5503	5820	-5.8
14	160	100	5663	5920	-4.5
15	162	20	5825	5940	-2.0
16	163	180	5988	6120	-2.2
17	360	340	6348	6460	-1.8
18	131	130	6479	6590	-1.7
19	228	165	6707	6755	-0.7
20	280	500	6987	7255	-3.8
21	320	340	7307	7595	-3.9
22*	408	390	7715	7985	-3.5

* After cycle 21, the resin was stripped according to the Mintek procedure (18), see text.

0700A

WD1

Table 14

NICKEL RECOVERIES DURING CYCLIC TESTWORK, COLUMN I

Cycle	Nickel Loaded mg	Nickel Recovered mg	Cumulative Nickel Loaded mg	Cumulative Nickel Recovered mg	Cumulative Nickel % Remaining on Resin
1	35.8	22.7	35.8	22.7	36.6
2	15.0	19.6	50.8	42.3	16.7
3	15.2	21.2	66.0	63.5	3.8
4	15.0	12.8	81.0	76.3	5.8
5	13.3	5.4	94.3	71.7	13.4
6	10.7	21.4	105.0	103.0	1.9
7	13.2	8.0	118.2	111.0	6.1
8	10.8	13.2	129.0	124.2	3.7
9	12.1	10.0	141.1	134.2	4.9
10	10.2	9.2	151.3	143.4	5.2
11	9.4	8.6	160.7	152.0	5.4
12	9.5	9.1	170.2	161.1	5.3
13	9.5	8.6	179.7	169.7	5.6
14	7.3	8.4	187.0	178.0	4.8
15	7.5	41.0	194.5	219.0	-12.6
16	7.5	-30.0	202.0	189.0	6.4
17	16.9	14.9	218.9	203.9	6.8
18	8.7	9.0	227.6	212.9	6.5
19	13.2	26.5	240.8	239.4	0.6
20	5.7	5.5	246.5	244.9	0.6
21	7.2	3.9	253.7	248.8	1.9
22*	6.5	1.3	260.2	250.1	3.9

* After cycle 21, the resin was stripped according to the Mintek procedure (18), see text.

0700A

WD1

However, for cycles 5 to 8, when the acid and WDI/Lac reagents were varied, it can be seen that lowering the acidity to 0.03 M acid, or decreasing the concentration of WDI/Lac reagent by a factor of 0.3 had a detrimental effect on the recovery of nickel from the resin (cycles 5 and 7). However, 0.1 M acid and approximately 0.5 times the "optimal" concentration of WDI/Lac reagent appeared to be sufficient for the recovery of nickel (cycles 6 and 8).

For cycle 14, when the regenerant solution from cycle 13 was retained and reused, the percentage of nickel stripped did not decrease, as opposed to that observed for Cu and Zn. The same regenerant solution was used for cycle 15 and part of the strip during cycle 16, after which it was replaced with fresh regenerant. Unfortunately, the assay for Ni in the cycle 15 regenerant appears to be in error. The same regenerant, after being reused for part of the cycle 16 elution had a lower Ni content than after stripping cycle 15. Fortunately, since the same regenerant was reused for part of cycle 16, the excessive amount of nickel apparently recovered during cycle 15, was subtracted from the cumulative sum after the regenerant was reassayed after cycle 16.

Iron

As opposed to the three other base metals discussed, iron showed definite resin-poisoning behaviour. After 20 cycles, 34 mg of Fe had been loaded on the resin, and only 2.8 mg had been removed during regeneration: 92% of the iron remained on the resin (see Table 15).

Table 15

IRON RECOVERIES DURING CYCLIC TESTWORK, COLUMN I

Cycle	Iron Loaded mg	Iron Recovered mg	Cumulative Iron Loaded mg	Cumulative Iron Recovered mg	% Remaining on Resin
1	4.33	0	4.33	0	100
2	2.36	0.10	6.69	0.10	98.5
3	2.36	0.12	9.05	0.22	97.6
4	0.04	0.10	9.09	0.32	96.5
5	0.15	0.23	9.24	0.55	94.0
6	0.18	0.17	9.42	0.72	92.4
7	-0.12	0.43	9.30	1.15	87.6
8	-0.04	0.39	9.26	1.54	83.3
9	3.87	0.06	13.13	1.60	87.8
10	0.48	0.13	13.61	1.73	87.3
11	0.76	0.15	14.37	1.88	86.9
12	0.70	0.16	15.07	2.04	86.5
13	0.68	0.13	15.75	2.17	86.2
14	0.06	0.01	15.81	2.18	86.2
15	0.08	0.02	15.89	2.20	86.2
16	0.14	0.18	16.03	2.38	85.1
17	0.92	0.13	16.95	2.53	85.1
18	2.27	0.07	19.22	2.60	86.5
19	3.98	0.06	23.20	2.66	88.5
20	10.84	0.11	34.04	2.77	91.9
21	7.44	n.a.	41.48	-	-
22*	10.64	n.a.	52.12	-	-

* After cycle 21, the resin was stripped according to the Mintek procedure (18), see text.

0700A

The variance in the amount of iron loaded during each cycle was dependent on the amount of Fe present in the feed effluent solution, which varied somewhat throughout the testwork. For the cycles which showed significantly higher loadings of Fe (cycles 18 to 21 and cycle 9), the waste effluent solution assayed higher in Fe (1.5 to 3.5 mg Fe/L) than the other cycles, for which the feed effluent solution assayed 0.15 mg/L Fe (cycles 4 to 8 and 14 to 16) or approximately 0.5 mg/L Fe (cycles 10 to 13 and 17).

Cyanide

Since the primary function of column I is to remove all metal cyanide complexes from the waste effluent solution, no attempt was made to quantify the removal and recovery of cyanide throughout the 21 cycles. The amount of cyanide not removed from the resin during each cycle can be estimated from the metals analyses and recoveries. Only iron acted as a poisoning agent, and iron was present in the feed solution at very low concentration (5 mg/L).

However, for cycle 1 the cyanide loading and recovery was followed in order to confirm the cyanide recoveries reported in Appendix III Sections 2.2 and 2.3 above. The amount of cyanide loaded on the resin prior to stripping during cycle 1, was 1564 mg CN(t) (135 mg CN/g resin). The amount of cyanide recovered in the alkaline trap (NaOH, pH 12) after 7 hours of stripping with the WDI/Lac regenerant, was 1463 mg CN(t), or 93.5% of the cyanide. This is in agreement with the data provided in the previous sections. The stripping data for cycle 1 is presented in Figure 16.

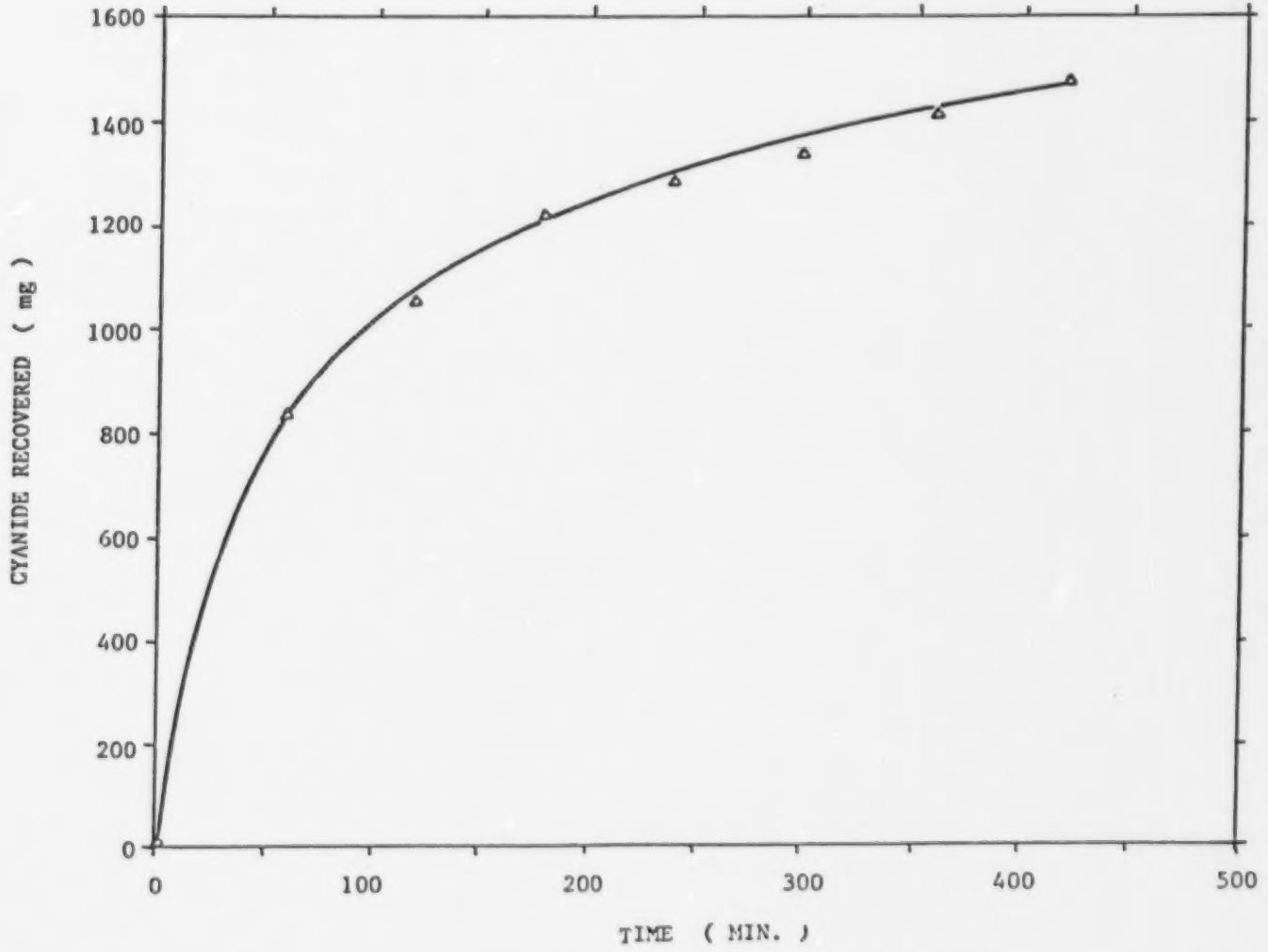


FIGURE 16 : CYCLE 1 RECOVERY OF CYANIDE IN CAUSTIC TRAP

WD1

For cycles 14 to 21, the same caustic solution remained in the trap, and the cyanide concentration in the trap reached 6000 mg/L CN(t). For these cycles, a second trap (200 mL; pH 12 NaOH) was added to recover any cyanide, should the efficiency of the first alkaline trap decrease with increasing concentrations of NaCN. In all cases, less than 1% of the cyanide was recovered in the second trap.

In a plant situation, the cyanide concentration in the alkaline trap would be built up to the point where the alkaline solution was no longer trapping 99% of cyanide. Alternatively, two traps could be used in sequence, and the cyanide concentration of the first could be increased to either the point of saturation, or to the point where the second trap began to loose its efficiency, whichever came first. At this point, the solution in the first trap would be recycled to the leach circuit, trap 2 would become trap 1, and a fresh alkaline solution would be added as trap 2. As already mentioned above, a portion of the column effluent from column I, containing only free cyanide and lime, could be used rather than fresh water and NaOH. In this case, however, the formation of $CaCO_3$ would require attention.

Overall Loss in Loading Capacity

The cumulative metals (Cu + Zn + Ni + Fe) loaded on the resin for each cycle is provided in Table 16. Initially, the capacity observed for loading 4 L of mill effluent was 1209 mg of metals/25 mL resin (105 mg/g resin). After 8 cycles, the apparent capacity was 1109 mg/25 mL resin (96 mg/g resin), or about 91% of the capacity of fresh resin. After 20 cycles, the apparent capacity had dropped to 633 mg metals/25 mL resin (55 mg/g resin) or about 52% of the initial capacity.

0700A

Table 16

CYCLIC TESTWORK: AMOUNT OF WASTE EFFLUENT TREATED

CONCENTRATION OF REGENERANT SOLUTION

Cycle	Volume Feed Effluent L	Regenerant Solution Acidity M	Regenerant Solution WDI/Lac Reagent Optimal x Factor	Cumulative Metals Loaded mg
1	-	0.1	x 1	1869
2	4	0.1	x 1	1209
3	4	0.1	x 1	1293
4	4	0.1	x 1	1103
5	3	0.03	x 0.3	1024
6	2.5	0.1	x 0.6	886
7	4	0.1	x 0.3	1109
8	4	0.1	x 0.4	1039
9	3	0.1	x 0.7	1033
10	2	0.1	x 0.7	598
11	2	0.2	x 0.7	612
12	2	0.2	x 0.7	631
13	2	0.2	x 0.7	647
14	1.5	0.2	x 0.7	452
15	1.5	0.2	x 0.7	461
16	1.5	0.2	x 0.7	463
17	4	0.2	x 0.7	750
18	1.5	0.2	x 0.7	441
19	2.65	0.2	x 0.7	635
20	4	0.2	x 0.7	633
21	4	0.2	x 1.4	674
22*	4	0.2	x 1.4	854
New Resin	4	-	-	708

* After cycle 21, the resin was stripped according to the Mintek procedure (18), see text.

0700A

However, the assay data had implied that only Fe had accumulated on the resin, and only to 31 mg Fe/25 mL resin (2.7 mg Fe/g resin); not enough poisoning had occurred to account for the observed loss in loading capacity.

Effluent A does not contain detectable levels of Pb, As, Sb, Hg or Co. The only other species present was thiocyanate. Thiocyanate could affect the observed loading capacity in two ways. If the concentration of SCN in effluent A varied significant from batch to batch, and if thiocyanate loads efficiently on the resin, then the apparent loading capacity, based only on base metals, would vary according to the thiocyanate concentration in the feed. The second way in which thiocyanate could affect the observed loading capacity would be if thiocyanate acted as a poisoning agent. This second possibility was eliminated by the work reported in Section 4.0 of Appendix III below, which indicated that thiocyanate is efficiently removed during the elution process.

In a paper published by C.A. Fleming of Mintek (18), a stripping/regeneration procedure for removal of Au, Ag, Co, Ni, Zn and Fe cyanide complexes from strong base resins was reported. This stripping procedure was advocated for recovery of aurocyanide from strong base resins, since $Au(CN)_2^-$ is not efficiently removed from strong base resins using acids or salts. The process is a two stage elution-regeneration procedure. The gold and all of the base metals are removed from the resin using NH_4SCN. The NH_4SCN in turn is removed from the resin using Fe(III) (as the sulphate or nitrate), returning the resin to the sulphate or nitrate forms, respectively.

Our interest in this procedure was two-fold. First of all, it implied that thiocyanate is not readily removed from strong base resins by elution with H_2SO_4, instead, Fe (III) had to be used. This led us to suspect that perhaps thiocyanate might be poisoning our resin. Secondly, the Mintek strip for aurocyanide (1.0 M NaOH: 2 M NH_4SCN) recovered greater than 90% of Cu, Fe, Ni, Co and Zn from resin loaded with metal cyanide complexes and might be used to remove any residual metals from the resin accumulated during the cyclic testwork.

We decided to investigate the Mintek strip in two stages. First, Fe(III) as $Fe(NO_3)_3$ was passed through the resin after cycle 20 was finished (resin loaded and stripped). The eluate was assayed for thiocyanate to ascertain the amount removed from the resin by the Fe(III). The resin was then reloaded during cycle 21 to determine if the loading capacity had been restored by the removal of thiocyanate.

The Fe^{3+} solution (480 mL; 0.08 M Fe(III)) contained only 37.5 mg/L SCN (0.0006 M) after passage through the "poisoned" resin. Fleming (18) observed that the concentration of thiocyanate emerging from the column in the eluate was constant in the initial bed volumes. Typical concentrations for regeneration of resin poisoned with thiocyanate using 0.1 M Fe(III) were of the order of 0.5 M SCN. The extremely low level of thiocyanate in the eluate implied that the cyclic resin was not poisoned with thiocyanate.

The conclusion that thiocyanate did not cause our loss in capacity was confirmed when the resin was reloaded with effluent A during cycle 21, and the resin capacity was unaltered by our efforts.

0700A

WD1

As shown in Table 16, the capacity for total metals during cycle 21 was 675 mg metals/25 mL resin (58 mg/g resin), or about 56% of the initial capacity observed for cycle 2 (1209 mg/25 mL resin).

The second stage of testing using the Mintek procedure involved the full two stage elution-regeneration process, to see which metals, if any, were eluted by the Mintek strip. After the resin was stripped during cycle 21 according to the usual procedure (the highest concentrations of acid and WDI/Lac reagents were used), the resin was eluted using the 1.0 M NaOH, 2 M NH_4SCN eluant (500 mL) recommended by Mintek and then regenerated using $Fe_2(SO_4)_3$.

During elution with the initial 250 mL of the NH_4SCN/NaOH, a green sludge was removed from the column, followed by a blue solution. The column changed from a brown-yellow colour to green, and there appeared to be precipitation occurring within the resin bed. These solids were eluted from the resin after a further 250 mL of the NH_4SCN/NaOH eluate had passed through the column. The eluate, containing a substantial amount of solids was treated with HCl followed by HNO_3 in an attempt to dissolve the solids in order to assay a solution. The mixture changed from green/blue to orange to blood red to rusty brown. At this stage, a violent reaction began and a fair amount of the mixture was lost. The final solids were yellow. The pulp which remained, dissolved readily in sodium hydroxide and was assayed. Although the total amount of metals removed from the resin was not known, the proportions were as follows:

	Cu	Zn	Ni	Fe	Co	As	Sb	Hg	Mo
Concentration in NaOH solution, mg/L	45.0	0.2	2.5	11.7	6.0	0.08	0.05	0.02	0.004

0700A

Therefore, some Cu, Fe, Co and Ni were removed from the resin using the Mintek strip. The best way to ascertain the significance of the quantity removed, was to reload the resin, and observe if the loading capacity improved significantly.

To complete the Mintek strip, a solution of Fe(III) was passed through the column according to the procedure described by Fleming (18) in order to remove the thiocyanate from the resin. Then the resin was reloaded during cycle 22, to determine how much of the lost resin capacity had been restored. As shown in Table 16, the capacity for metals increased to 854 mg/25 mL resin (74 mg/g resin) or to 71% of the original capacity displayed for 4 L of feed effluent, an increase of 15% compared to cycle 21 which displayed 56% of the original capacity. Although some metals were remaining on the resin after the WDI/Lac stripping procedure (i.e. after cycle 20), only iron and cobalt were found to be true poisoning agents; the Cu and Ni had not accumulated on the resin. (More information is provided on cobalt in Appendix III Section 2.6 "Poisoning Agents".)

Since effluent A varied somewhat from pail to pail, it was decided to reload fresh resin (25 mL, sulphate form) with the effluent, (4 L) according to the procedure used during the cyclic testwork, to determine if the "apparent" loss in capacity was real. The loading capacity of fresh resin using the current supply of effluent A was: 508 mg Cu; 176 mg Zn; 11.5 mg Fe and 12.2 mg Ni, for a total loading of 708 mg metals/25 mL (see Table 8). This is slightly lower than the capacity observed during cycle 22 indicating that prior to cycle 22, the resin had the same capacity as fresh resin. Therefore, it is concluded that the observed decrease in capacity was not due to poisoning of the resin other than by cobalt and iron, but due to a change in the composition of the feed effluent solution, other than the concentrations of Cu, Fe, Ni and Zn.

0700A

An increase in the total ionic strength of the feed effluent, would for example, affect the equilibrium established between feed solution and the resin during loading.

As a final confirmation that there was no overall loss in resin capacity, the resin used during the cyclic tests was assayed for most elements. The results are provided below:

Resin Analyses %

Co	Cu	Fe	Hg	Mo	Ni	Pb	Zn	CN_T
0.018	0.001	0.39	0.001	0.0005	0.002	0.13	0.008	0.18

A.III.2.6 Resin Poisoning Agents

Effluent A, which was used for the cyclic testwork, did not contain detectable levels of antimony, arsenic, cobalt, mercury or molybdenum. Therefore, it was not known if anionic exchange resins would remove these metals efficiently from cyanide waste effluent, and if so, if they could be recovered from the resin using the same elution process as was used for the base metals.

A.III.2.6.1 Adsorption/Elution Testwork using Enriched Cyanide Waste Effluent

Since none of the waste effluents received contained high levels of all of the above metals, effluent A was enriched by the addition of each of these metals. The metals were added to the effluent either as the cyanide or oxide complexes typical of cyanide waste effluents, $Co(CN)_6^{3-}$, As_2O_3, Sb_2O_3, $(NH_4)_6Mo_7O_{24}$ or as simple salts ($HgCl_2$). Cyclic testwork was carried out as described above for the as-received effluent A (Appendix III Section 2.5).

The resin (25 mL of Lewatit MP-500, sulphate form) was loaded and eluted eight times. During loading, 40 bed volumes (1 L) of the enriched effluent A was passed through the resin bed per cycle. A composite sample of the feed solution, and the column effluent were assayed for As, Co, Hg, Mo and Sb to determine the amount of each metal loaded during each cycle.

After each loading cycle, the resin was eluted with the WDI/Lac regenerant solution. The regenerant solution was recirculated through the resin bed for 6 hours. Samples were taken at 1 hour intervals.

The results are presented in Table 17 and are discussed below for each metal.

Antimony

During the first cycle, the resin (11.55 g of MP-500, sulphate form) removed antimony from the feed effluent (13.1 mg/L Sb; 1 L) down to 1.5 mg/L, loading the resin to a level of 1 mg Sb/g resin. After the first cycle, progressively less antimony loaded onto the resin. After eight cycles, antimony had accumulated to 1.7 mg Sb/g resin.

The first elution cycle recovered 7 mg Sb, leaving 39% of the antimony on the resin, and very little was recovered during subsequent elution cycles. After eight cycles, 66% of the antimony which had been removed from the enriched effluent remained on the resin bed.

In summary, antimony does not load very efficiently in the presence of base metals, and is not eluted efficiently from the resin using the WDI/Lac regenerant. Antimony accumulates on the resin bed.

0700A

Table 17

CYCLIC TESTWORK USING ENRICHED CYANIDE WASTE EFFLUENT

Metal	Cycle	Metal Loaded mg	Metal Recovered mg	Cumulative Metal		
				Loaded mg	Recovered mg	% Remaining on resin
Sb	1	11.6	7.1	11.6	7.1	39
	2	3.6	0.6	15.2	7.7	49
	3	11.0	1.9	26.2	9.6	63
	4	1.0	0	27.2	9.6	65
	5	0.6	0.6	27.8	10.2	63
	6	1.6	0	29.4	10.2	65
	7	0.4	0	29.8	10.2	66
	8	0.5	0	30.3	10.2	66
As	1	0.3	1.3	0.3	1.3	-
	2	1.6	3.2	1.9	4.5	-
	3	1.8	3.2	3.7	7.7	-
	4	0.7	0	4.4	7.7	-
	5	0	0	4.4	7.7	-
	6	0.1	0.4	4.5	8.2	-
	7	1.0	0.8	5.5	9.0	-
	8	0	0.1	5.5	9.1	-
Co	1	16.6	0.08	16.6	0.08	99.5
	2	16.4	0.09	33.0	0.17	99.5
	3	15.7	0.07	48.7	0.24	99.5
	4	14.4	0.07	63.1	0.31	99.5
	5	13.6	0.04	76.7	0.35	99.5
	6	10.8	0.06	87.5	0.41	99.5
	7	12.2	0.05	99.7	0.46	99.5
	8	10.9	0.05	110.6	0.51	99.5

0700A

WDI

Table 17 cont.

CYCLIC TESTWORK USING ENRICHED CYANIDE WASTE EFFLUENT

Metal	Cycle	Metal Loaded mg	Metal Recovered mg	Cumulative Metal Loaded mg	Cumulative Metal Recovered mg	% Remaining on resin
Hg	1	20.8	0.2	20.8	0.2	99
	2	23.8	4.0	44.6	4.2	91
	3	19.0	3.8	63.6	8.0	88
	4	15.8	7.4	79.4	15.4	81
	5	14.7	4.9	94.1	20.3	78
	6	16.8	1.4	110.9	21.7	80
	7	11.7	1.7	122.6	23.4	81
	8	0.6	0	123.2	23.4	81
Mo	1	19.7	3.0	19.7	3.0	85
	2	-4.5	2.1	15.2	5.1	66
	3	1.5	1.8	16.7	6.9	59
	4	2.3	1.3	19.0	8.2	57
	5	1.0	1.4	20.0	9.6	52
	6	3.1	1.3	23.1	10.9	53
	7	1.3	1.0	24.4	11.9	51
	8	6.1	1.8	30.5	13.7	55

0700A

Considerably more loading testwork was carried out on antimony once cyanide waste effluent from one of the Hemlo sites was received. See Appendix III Section 2.7 for the results of this testwork.

Arsenic

During the first loading cycle, the arsenic concentration of the enriched effluent (2.53 mg/L As; 1 L) was reduced slightly to 2.26 mg/L As; arsenic loaded on the fresh resin to only 0.02 mg As/g resin. Therefore, arsenic was not removed efficiently from cyanide waste effluent by the sulphate form of Lewatit MP-500.

The elution testwork was inconclusive. The regenerant solution typically contained < 1 mg/L arsenic. However, for most cycles more arsenic apparently was recovered than had been loaded on the resin. It was determined that the problem was due to inaccurate arsenic analyses when below the 1 mg/L level. Fortunately, this problem was discovered and corrected prior to the testwork which was carried out subsequently on mill effluent from the Hemlo area (see Appendix III Section 2.7 for results of arsenic testwork).

Cobalt

During the first loading cycle, cobalt in the enriched effluent (17 mg/L; 1 L) was reduced to 0.39 mg/L in a composite sample of the first 40 bed volumes of the column effluent. Therefore, fresh resin loaded cobalt to 1.44 mg Co/g resin under these conditions.

During each subsequent cycle, progressively less cobalt was removed from the enriched effluent by the anionic resin. After eight cycles, the resin was loaded to 9.5 mg Co/g resin, and was not yet loaded to capacity.

During elution, the concentration of cobalt in the regenerant solution never exceeded 0.15 mg/L Co. After eight cycles, 99.5% of the cobalt remained on the resin.

Cobalt is clearly a resin poisoning agent. Further testwork was carried out on the elution of cobalt from resins (see Appendix III Section 2.6.3).

Mercury

Mercury in the enriched effluent assayed 20.6 mg/L. During the first load cycle, the composite column effluent sample assayed below the detection limit (< 0.02 mg/L Hg), indicating that Hg had been loaded to 1.8 mg/g resin. After the first two cycles, the amount of mercury loaded during each stage gradually decreased. During the eighth cycle, only 0.6 mg of mercury was removed from the enriched effluent. At this point, the resin was loaded to 8.6 mg Hg/g resin.

The first elution cycle recovered only 1% of the mercury. As the amount of mercury loaded on the resin increased, the amount recovered during elution improved. However, once the resin became saturated with mercury, the elution efficiency dropped to zero as well. After eight cycles, mercury no longer was loaded by nor eluted from the resin. At this point 81% of the mercury which had been removed from the enriched effluent remained on the resin.

Molybdenum

The enriched effluent contained 28.2 mg/L molybdenum. After 40 bed volumes (1 L) of the effluent had passed through the resin bed, a composite sample of the column effluent assayed 8.5 mg/L molybdenum. Molybdenum was loaded to 1.7 mg/g resin. During the second loading cycle, some molybdenum was displaced from the resin by other complexes. During subsequent cycles, small amounts of molybdenum were removed from the enriched effluent solution. After eight cycles, the resin was loaded to 1.5 mg Mo/g resin.

During the first elution cycle, the molybdenum concentration in the regenerant solution reached 3.8 mg Mo/L after 6 hours. Eighty-five percent of the molybdenum remained on the resin. During some of the subsequent cycles, more molybdenum was removed from the resin than was loading, reducing the percent remaining on the resin to 55% after eight cycles.

Table 18 summarizes the effectiveness of Lewatit MP-500 in the sulphate form for removal of antimony, arsenic, cobalt, mercury and molybdenum from the enriched effluent.

Table 18

REMOVAL OF Sb, As, Co, Hg AND Mo FROM MILL EFFLUENT

Metal	Sb	As	Co	Hg	Mo
Efficiency:					
Loading	No	No	Yes	Yes	No
Elution	No	-	No	No	No

0700A

Cobalt and mercury were loaded efficiently, producing barren levels in the 40 bed volume composite samples of only 0.4 mg Co/L and 0.02 mg Hg/L, and loading to 9.6 and 8.6 mg metal/g resin, respectively, after eight cycles (200 bed volumes). The other three metals were not removed efficiently from the waste effluent, leaking greater than 1 mg/L of the metal in the 40 bed volume composite sample of column effluent.

In an attempt to find a form of ion exchange resin which would successfully remove antimony and arsenic from cyanide waste effluent, a number of further tests were carried out on mill effluent from one of the Hemlo sites. The results of this loading work is provided in Appendix III Section 2.7. Since the Hemlo solution did not contain high levels of molybdenum (0.37 mg Mo/L effluent) no further testwork was carried out on this metal.

Table 18 above also includes a summary of the elution results. The elution process which was found to be effective for the recovery of copper, nickel and zinc from the resin, was not effective at removing antimony, cobalt, mercury or molybdenum from the resin. The two most common resin poisoning agents, iron and cobalt, were studied in further elution testwork below (see Appendix III Section 2.6.2 and 2.6.3).

A.III.2.6.2 Removal of Iron Cyanides from Strong Base Resins

During the cyclic testwork (see Appendix III Sections 2.5 and 2.6.1), iron was identified as a poisoning agent, i.e. iron loaded on the resin but was not removed during the elution process. The Mintek (18) strip, referred to in Appendix III Section 2.5, is effective at eluting 97% of ferri and ferrocyanides loaded on a strong base resin. This stripping procedure, which uses thiocyanate to remove iron as various iron thiocyanate complexes, $Fe(SCN)_n$, leaves the resin in the thiocyanate form. A subsequent regeneration step is required. Ferric sulphate is passed through the column and converts the resin back to the sulphate form by removing the thiocyanate as iron thiocyanate complexes. The iron, being a cation, does not reload onto the resin.

Only a small portion of the resin capacity was poisoned by iron during the cyclic testwork. In order to investigate the Mintek process more carefully, and to compare it to other potential stripping agents for iron cyanides, a series of six tests were carried out using resin (10 mL, Lewatit MP-500 sulphate form) which had been loaded with a 50:50 mixture of potassium ferrocyanide and potassium ferricyanide.

In addition to checking the NH_4SCN/NaOH method advocated by Mintek, NH_4Cl, $(NH_4)_2SO_4$, $NaHCO_3$, $NH_4O_2C_2H_3$ and citric acid were tested. In all cases, two 50 mL portions of the eluant were pumped downflow through the resin bed. Each 50 mL sample of eluate was assayed for iron. The amount of iron loaded on the resin, the concentration of the various eluants tested, and the results of the stripping testwork are provided in Table 19.

Table 19

ELUTION TESTWORK ON THE REMOVAL OF IRON CYANIDE COMPLEXES FROM STRONG BASE RESIN

Test	Eluant	Iron on Resin mg	Iron Recovered in Eluate, mg		
			First 50 mL	Second 50 mL	Total Percent
1	1 M NH_4SCN 0.5 M NaOH	4.76	4.1	0.73	101
2	1 M NH_4Cl 0.5 M NaOH	4.75	0.04	0.12	3.4
3	1 M $(NH_4)_2SO_4$ 0.5 M NaOH	4.59	0.028	0.023	1.1
4	1 M $NaHCO_3$ 0.5 M NaOH	4.54	0.018	0.025	0.95
5	1 M $NH_4O_2C_2H$ 0.5 M NaOH	4.50	0.006	0.006	0.26
6	1 M Citric Acid 1 M NaOH	4.49	0.022	0.023	1.0

The Mintek eluant was far superior to the other eluants tested. One hundred percent of the iron was removed from the resin in 10 bed volumes of eluate.

For waste effluent solution containing low levels of iron cyanides, the resin bed could be eluted periodically using this method. The eluate, containing iron thiocyanates, can be treated with any alkali or base. The iron will precipitate from the solution as ferric hydroxide and may be filtered, redissolved in sulphuric or nitric acid and recycled to the regeneration stage. The filtrate, containing thiocyanate may be recycled to the elution step. In this manner, Mintek has shown this procedure to be efficient and economical; the overall consumption of thiocyanate and ferric ions is theoretically zero.

A.III.2.6.3 Removal of Cobalt Cyanide from Strong Base Resins

The cobalt cyanide complex, $Co(CN)_6^{3-}$ is known to be strongly bound by anionic exchange resins and has been identified as one of the most difficult complex cyanides to elute. Since effluent A had no detectable level of cobalt (< 0.004 ppm), a synthetic solution of $Co(CN)_6^{3-}$ was prepared and used to load Lewatit MP-500 resin in preparation for elution testwork. Cobalt (II) sulphate heptahydrate (1.0 g) was dissolved in a solution of sodium cyanide (1.8 g NaOH; pH 11; 60 mL). Air was drawn through the moss green solution for 1 hour. The solution turned yellow within minutes, indicating the presence of hexacyanocobalt (III). The solution was diluted to 500 mL and 115 mL was passed through a column containing 6.5 mL of Lewatit MP-500 in the sulphate form. Solution analyses indicated that the 35.1 mg of cobalt had been loaded, or 11.7 mg Co/g resin.

In order to confirm that the Mintek strip does remove cobalt from the resin, a solution of 1M NH_4SCN, 0.5 M NaOH was passed through the resin bed. Samples were collected and assayed. The results are provided in Figure 17. After 12 bed volumes of eluant had passed through the resin bed, 93% of the cobalt had been recovered; 100% was recovered within 20 bed volumes.

While the Mintek (18) process is recommended for the periodic removal of cobalt and iron, the WDI/Lac process is recommended for the routine elution of copper, nickel and zinc. The latter typically are present in much higher concentrations in waste effluent streams and occupy the bulk of the resin capacity. The WDI/Lac process utilizes inexpensive reagents, and is a one-step process: elution returns the resin to the active form, no separate regeneration stage is required.

0700A

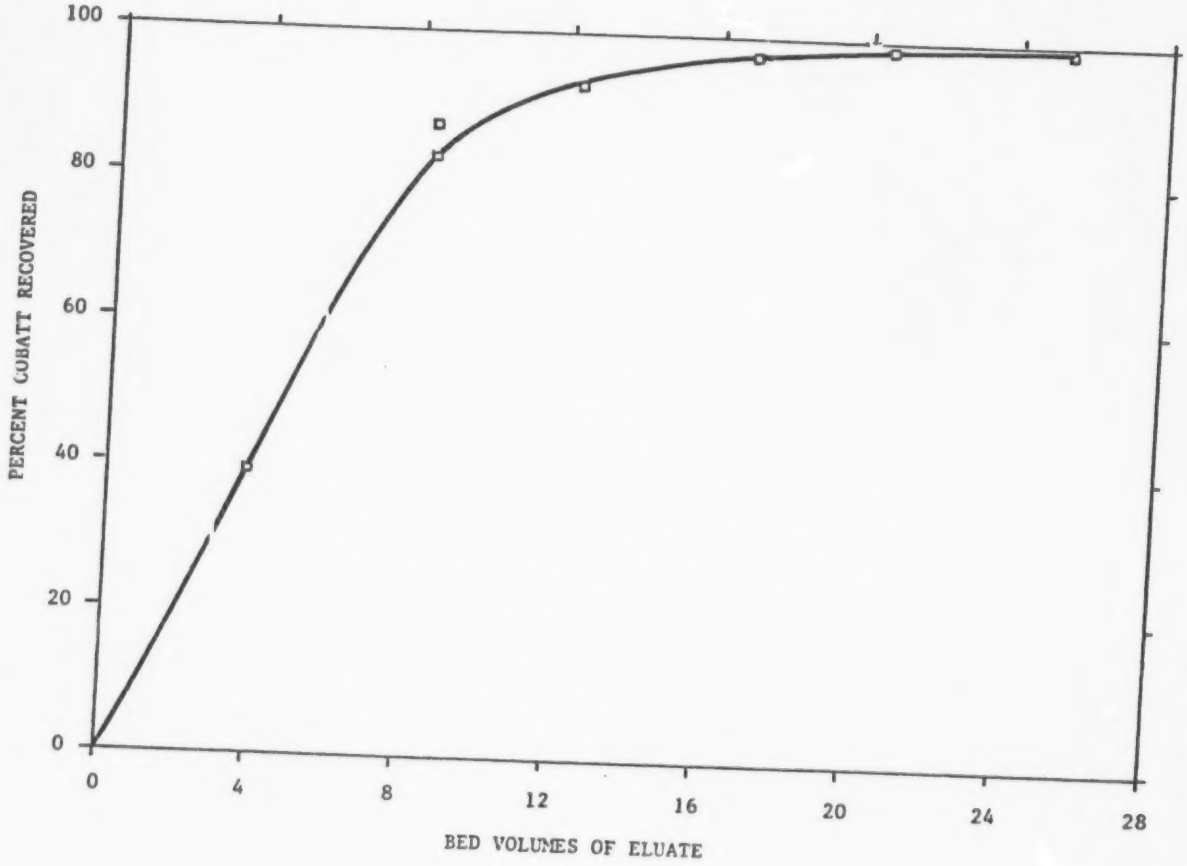


FIGURE 17: COBALT RECOVERY FROM RESIN USING NH_4SCN / NaOH

A.III.2.7 Removal of Antimony and Arsenic from Mill Effluent Using Ion Exchange Resins

Once the effluent from the Hemlo site was received, further loading tests were carried out in an attempt to find an ion exchange resin which would remove arsenic and antimony to low levels ($\leq$ 0.1 ppm). Effluent was received in three shipments and from various locations on site (leach tank 4, leach tank 6, tailings pond and reclaim water). Therefore, the head assay varied somewhat from test to test. The bulk of the work was conducted on tailing pond effluent, which assayed 35 mg/L Sb and 1 to 2 mg/L As. In addition, while waiting from the Hemlo solution, two tests (tests 3 and 4) were carried out on effluent received from another site, effluent C, which assayed 2 to 3 mg/L Sb and 9 mg/L As. Because of this variance, the head assay is provided for each test.

The first five tests were carried out in columns. However, it soon became apparent that the initial screening of resins for antimony and arsenic removal would require extensive work, and the procedure was changed to the batch contact method using agitated vessels.

In total, thirty-three tests were carried out. The results are discussed below.

Tests 1 to 5

For tests 1 to 5, five different resins were investigated for the removal of antimony and arsenic from cyanide waste effluent. These tests were carried out downflow in a column.

Three forms of Lewatit MP-500 strong base, macroporous) were investigated, the sulphate, hydroxide and chloride forms. The sulphate form of Amberlite IRA-400 (strong base, gel) was tested. Dowex 50W-X8 (strong acid, gel, sodium form) was included since the speciation of the arsenic and antimony compounds in cyanide waste effluent is unknown. The results are presented in Table 39.

For the Lewatit MP-500 resins (Tests 1 to 3) the hydroxide form performed the best, removing arsenic to below the detection limit (0.08 mg/L) and loading antimony to 2.3 mg Sb/mL resin after 40 bed volumes. The chloride form of MP-500 and the sulphate form of IRA-400 were tested using effluent C. Neither resin removed antimony or arsenic efficiently from the effluent, after passage of 10 and 40 bed volumes of effluent, respectively.

The cationic exchange resin (test 5) had no effect on the antimony or arsenic concentrations, indicating that these metals are not present to any significant extent as cationic compounds.

Table 20

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT: TESTS 1-5

Test*	Resin Type, form	Resin Vol. mL	Effluent Bed Volumes	Antimony Solution, mg/L Feed	Antimony Solution, mg/L DX**	Antimony Loading mg/mL resin	Arsenic Solution mg/L Feed	Arsenic Solution mg/L DX**	Arsenic Loading mg/mL resin
1	MP-500 SO_4	25	40	56.0	54.1	0.08	2.4	1.1	0.05
2	MP-500 OH	25	40	76.4	19.2	2.3	2.6	<0.08	0.10
3	MP-500 Cl	15	10	2.7	1.4	0.01	8.3	0.2	0.08
4	IRA-400 SO_4	25	40	2.1	1.8	0.01	9.5	6.8	0.11
5	50W-X8	10	10	62.2	62.1	0	2.0	2.0	0

* All five tests were column tests
** column discharge

Tests 6 to 9

For a more direct comparison, using the same head solution (Hemlo tailing pond effluent) a series of batch contact tests was carried out on four of the resins tested above, Lewatit MP-500 in the sulphate, hydroxide and chloride forms and Dowex 50W-X8, sodium form. The resin was contacted in a beaker five times with 100 mL samples of the effluent solution. The solution was assayed after each contact for antimony and arsenic. See Table 21 for the results.

Once again, the hydroxide form of MP-500 performed the best at removal of antimony. Antimony loaded to 1 mg Sb/mL resin after 50 bed volumes, and had not yet attained equilibrium capacity. The other three resins showed very low capacities for antimony, loading to only 0.15 mg Sb/mL resin and reaching equilibrium capacity very quickly. The arsenic head assay was very low. The sulphate form of MP-500 showed very low affinity for arsenic. The hydroxide and chloride forms removed arsenic to below the detection limit.

Since the hydroxide form of Lewatit MP-500 looked the most promising of the resins tested, it was chosen for further loading capacity testwork.

Table 21

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT USING ION EXCHANGE RESINS: TESTS 6 TO 9

Test	Resin Type form	Resin Vol. mL	Effluent Bed Volumes*	Antimony Solution, mg/L Feed	Antimony Solution, mg/L DX**	Antimony Loading mg/mL resin	Arsenic Solution mg/L Feed	Arsenic Solution mg/L DX**	Arsenic Loading mg/mL resin
6	MP-500 SO_4	10	10	34.4	26.7	0.08	1.1	0.18	0.019
			20		32.5	0.10		0.22	0.018
			30		32.5	0.12		0.39	0.025
			40		30.7	0.15		0.44	0.032
			50		33.3	0.16		0.40	0.039
7	MP-500 OH	10	10	32.5	12.0	0.20	0.29	<0.08	0.003
			20		6.5	0.46		<0.08	0.006
			30		15.7	0.54		<0.08	0.009
			40		7.2	0.79		<0.08	0.012
			50		12.7	0.99		<0.08	0.015
8	MP-500 Cl	20	10	37.6	13.7	0.12	1.66	<0.08	0.008
			20		32.9	0.14		<0.08	0.017
			30		35.6	0.15		<0.08	0.025
			40		36.1	0.16		<0.08	0.033
			50		36.7	0.16		<0.08	0.042
9	50W-X8 Na	10	10	29.3	25.4	0.04	<0.08	<0.08	-
			20		29.1	0.04		<0.08	-
			30		20.8	0.13		<0.08	-
			40		30.0	0.12		<0.08	-
			50		29.7	0.12		<0.08	-

* Cumulative bed volumes
** Column discharge

Test 10

Although antimony loaded on to the resin, the efficiency was poor. In test 7, batch-contact resulted in loadings of only 1 mg Sb/mL resin after 50 bed volumes. In order to determine how much resin would be required to remove antimony to low levels, and to determine the corresponding resin loadings, a 200 mL sample of effluent was treated three times with fresh resin (20 mL resin/contact). The results are shown in Table 22.

After 10 bed volumes, batch contact, the resin was loaded to 0.20 mg Sb/mL resin, in agreement with the results of test 7, and the column effluent still assayed 15.3 mg/L antimony. After two more contacts with 20 mL of resin, the column effluent still assayed 0.72 mg/L antimony. Although continued contact with resin would mostly likely remove antimony to acceptable barren levels, the loading efficiency is poor: 60 mL of resin did not reduce 200 mL of effluent (3.3 bed volumes) to acceptable levels of antimony. Although in theory the hydroxide resin would work, the size of the columns required and the operating efficiency of the columns would make this process unacceptable.

Table 22

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT: TEST 10

	Resin			Antimony			Arsenic		
				Solution, mg/L			Solution mg/L		
Test	Type form	Vol. mL	Effluent Bed Volumes*	Feed	DX	Loading mg/mL resin	Feed	DX	Loading mg/mL resin
10	MP-500 OH	20	10	35.2	15.3	0.20	1.21	0.19	0.01
		20	(5)	15.3	3.97	0.11	0.19	<0.08	0.002
		20	(3.3)	3.97	0.72	0.003	<0.08	<0.08	0

0700A

Tests 11 and 12

Antimony and arsenic are typically present in much lower concentrations than the common base metals. When contacting the as-received effluent with resin, the bulk of the loading capacity of the resin is occupied by the other anions present in solution, due to their higher concentrations and affinity for the resin. Therefore, a scavenger column for antimony and arsenic removal was considered. From the previous testwork, a sulphate column to remove Co, Cu, Fe, Ni and Zn followed by an hydroxide column to remove Sb and As, seemed promising.

Tests 11 and 12 investigated the operation of these two columns in series. For test 11, 1 L of effluent was passed through a Lewatit MP-500 sulphate form column to remove base metals, and then through an hydroxide form column for removal of antimony and arsenic. Samples were taken periodically of the second column effluent (the volumes given in Table 23 for test 11 are cumulative volumes). The results were disappointing; antimony breakthrough occurred in less than 3 bed volumes. After 1 L (29 bed volumes) of effluent had passed through the two columns, the hydroxide form resin was loaded to near equilibrium capacity. The capacity of the hydroxide form of the resin for antimony, in the absence of base metals, was only 1.2 mg Sb/mL resin.

Table 23

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT:

TESTS 11 and 12

Test, Method	Resin Type form	Resin Vol. mL	Effluent Bed Volumes*	Antimony Solution, mg/L Feed	Antimony Solution, mg/L DX	Loading mg/mL resin
11 column	MP-500 SO_4	35	28.6	57.3	n.a.	-
	MP-500 OH	35	2.9		0.17	0.16
			5.7		0.31	0.33
			11.4		2.1	0.64
			14.3		6.0	0.79
			22.9		26.5	1.05
			28.6		51.7	1.21
12 batch	MP-500 OH	10	5 x 10 B.V.	27.7	n.a.	-
	MP-500 SO_4	10	10		8.96	0.19
			20		0.72	0.46
			30		9.17	0.64
			40		8.07	0.84
			50		4.14	1.07

For Test 12, the order of the two forms of the resin was reversed. The effluent was contacted first with MP-500 in the hydroxide form, followed by MP-500 in the sulphate form. This test was carried out batchwise using five 100 mL samples of effluent. Compared to tests 6 and 7, above, the order of contact performed better than the sulphate resin alone, and the results were very similar to those obtained using the hydroxide form of the resin alone.

It was concluded that the observed low capacity of the resin for antimony and arsenic was not due to competition for sites by the other base metal anions present in higher concentrations, but due to a low affinity of the resin for these complexes. At this point, Pourbaix diagrams for antimony and arsenic speciation in aqueous solution were consulted (20, 21). Both metals could exist in either the (III) or (V) oxidation state and may be present as a variety of oxides, hydrated oxides or hydroxides depending on the pH and redox potential.

According to the Pauxbaix diagrams, at pp 9 to 11, arsenic is thermodynamically stable as $HAsO_4^{2-}$ at zero and positive potentials, and as $H_2AsO_3^-$ or $HAsO_2$ at negative potentials. These compounds are large oxides with relatively low charge densities. Therefore, two explanations for the observed low affinity of the anionic exchange resins for arsenic and antimony were considered:

1. Although the speciation of arsenic and antimony compounds in cyanide waste effluent remains unknown, these complexes are most likely present as large hydrated oxides with low charge (monovalent or divalent) at the pH and redox potentials typical of mill effluent solutions. The resins have a low affinity for these compounds due to their low charge densities.

2. The compounds are so large as to not fit inside the pore of the macroporous bead of the resin, thereby reducing the effective operating capacity of the resin by limiting the compounds to loading on the surface of the resin head.

After discussions with three of the major resin manufacturers (Bayer-Lewatit, Dow, and Rohm and Haas), it was agreed that both explanations could be responsible for the observed low capacity for antimony and arsenic.

Both explanations were investigated. If the low affinity is due to a low charge density, the only way to increase the affinity of the antimony and arsenic compounds for the resin is to alter the form of the complexes themselves. Consequently, various tests were carried out altering the pH and redox potential of the feed solution, in an attempt to produce higher charge density anions, which might display a higher affinity for anionic exchange resins. The results of this work are discussed below.

Tests 13 to 20

For the following eight tests, the pH and oxidative potential of the cyanide effluent solution was altered in an attempt to improve the affinity of the anionic antimony and arsenic complexes for the resin by altering the composition of the antimony and arsenic species in solution. Hydrogen peroxide and manganese dioxide were used to adjust the potential, and sodium hydroxide or sulphuric acid was used to adjust the pH. In each case 20 mL of resin was contacted once for 1 hour with 100 mL of the adjusted cyanide effluent. The tests were carried out on both the sulphate and hydroxide forms of MP-500. The results are provided in Table 24.

Table 24

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT: TESTS 13 TO 20

Test	Resin - MP-500 Form	Vol. mL	Feed Solution Bed Vols.	pH	H_2O_2 g/L	MnO_2 g/L	Solution Analysis, mg/L Antimony Feed	Antimony DX	Arsenic Feed	Arsenic DX
13	SO_4	20	5	9	-	-	38.3	30.3	1.50	0.15
				9	2.2	-	38.3	30.1	1.50	0.13
				9	-	0.25	38.3	31.3	1.50	0.29
14	SO_4	20	5	10	-	-	36.7	30.9	1.33	<0.08
				10	9.4	-	36.7	30.6	1.33	<0.08
				10	-	0.25	36.7	30.4	1.33	<0.08
15	SO_4	20	5	11	-	-	36.7	30.8	1.41	<0.08
				11	9.4	-	36.7	31.2	1.41	<0.08
				11	-	0.25	36.7	30.6	1.41	<0.08
16	SO_4	20	5	12	-	-	35.8	29.4	1.24	<0.08
				12	2.2	-	35.8	30.0	1.24	<0.08
				12	-	0.25	35.8	29.0	1.24	<0.08
17	OH	20	5	9	-	-	38.3	9.15	1.50	<0.08
				9	2.2	-	38.3	9.50	1.50	<0.08
				9	-	0.25	38.3	8.90	1.50	<0.08
18	OH	20	5	10	-	-	36.7	9.34	1.33	<0.08
				10	2.2	-	36.7	8.98	1.33	<0.08
				10	-	0.25	36.7	8.32	1.33	<0.08
19	OH	20	5	11	-	-	36.7	9.47	1.41	<0.08
				11	2.2	-	36.7	9.65	1.41	<0.08
				11	-	0.25	36.7	8.61	1.41	<0.08
20	OH	20	5	12	-	-	35.8	12.2	1.24	<0.08
				12	2.2	-	35.8	12.2	1.24	<0.08
				12	-	0.25	35.8	11.9	1.24	<0.08

For tests 13 to 16, using the sulphate form of the resin, neither the pH nor the addition of oxidants had any effect on the loading of antimony, which loaded to 0.03 to 0.04 mg Sb/mL resin. Arsenic loaded best at pH 10 or above.

For tests 17 to 20, using the hydroxide form of the resin, arsenic loaded at all pH values tested. Antimony loaded to 0.14 to 0.15 mg Sb/mL resin at pH 9 to 11 with or without the addition of hydrogen peroxide or manganese droxide as oxidants. This capacity was reduced slightly, to 0.12 mg Sb/mL resin at pH 12; again no significant effect was noted by the addition of oxidants.

Tests 21 to 24

In a final attempt to produce a higher charge species, higher concentrations of hydrogen peroxide were added to the Hemlo effluent. For each test, 20 mL of resin (MP-500, hydroxde form) was contacted batchwise with 100 mL of the treated effluent for one hour. The concentration of hydrogen peroxide was increased from 0.72 to 36.0 g/L H_2O_2. As shown in Table 25, this increase in oxidative potential had no effect on the loading of either antimony or arsenic; antimony loaded to 0.13 mg/mL resin, and arsenic loaded to 0.005 mg/mL resin.

Table 25

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT: TESTS 21 TO 24

Test	Resin MP-500 Form	Resin MP-500 Vol. mL	Feed Solution Vol. L	Feed Solution pH	Feed Solution H_2O_2 g/L	Solution Analysis, mg/L Antimony Feed	Antimony DX	Arsenic Feed	Arsenic DX
21	OH	20	0.1	10	0.72	34.4	7.4	2.1	1.1
22	OH	20	0.1	10	7.2	34.4	7.5	2.1	1.2
23	OH	20	0.1	10	14.4	34.4	8.3	2.1	1.3
24	OH	20	0.1	10	36.0	34.4	7.7	2.1	1.2

Tests 25 to 29

Finally, in order to determine if the acid end of the pH scale might improve the situation, sulphuric, nitric and hydrochloric acids were used to drop the pH of the feed solution to about pH 8, or pH 3. The oxidative potential and pH of the resulting effluent were recorded. After 15 minutes, 100 mL of the effluent was treated batchwise with 20 mL of MP-500 resin in the hydroxide form. The head and final antimony and arsenic concentrations are provided in Table 26 . In all cases, the antimony loaded to 0.14 mg/mL resin and the arsenic to about 0.005 mg/mL resin. At this point, the approach of improving the affinity of the resin for arsenic and antimony by altering their speciation using pH and redox control was abandoned.

Table 26

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT: TESTS 25 TO 29

Test	Resin MP-500 Form	Resin MP-500 Vol. mL	Feed Solution Vol. mL	Feed Solution pH	Feed Solution Acid added	Feed Solution MV	Feed Solution H_2O g/L	Solution Analysis, mg/L Antimony Feed	Solution Analysis, mg/L Antimony DX	Solution Analysis, mg/L Arsenic Feed	Solution Analysis, mg/L Arsenic DX
25	OH	20	0.1	8.0	H_2SO_4	360	3.6	35.9	7.41	1.05	n.a.
26	OH	20	0.1	8.5	HNO_3	100	0	35.9	7.43	1.05	<0.08
27	OH	20	0.1	8.0	HCl	n.a.	0	35.9	7.49	1.05	<0.08
28	OH	20	0.1	3.2	H_2SO_4	480	0	35.9	7.72	1.05	<0.08
29	OH	20	0.1	3.0	HNO_3	500	0	35.9	8.61	1.05	0.13

Tests 30 to 33

The second possible explanation for the observed low capacity of the resin for antimony and arsenic was that the compounds were too large to fit inside the pore of the resin. There are two ways of overcoming this problem. Either obtain a larger pore size resin, or crush the beads. Although the first solution would be preferable, since crushing the bead would result in large pressure drops in a column, larger pore size beads were not obtained in time to included in Phase I of this program. However, two tests were carried out using ground Lewatit MP-500 (macroporous) and ground Amberlite IRA-400 (gel) resins. The tests were repeated with the unground resins for direct comparison.

Cyanide effluent (100 mL) was contacted batchwise with 5 mL of resin. The resin volumes were measured prior to grinding. The results are provided in Table 27 for Tests 21 and 22 using MP-500, and for Tests 23 and 24 using IRA-400. The results show that grinding does improve slightly the capacity of the macroporous resin, but had little effect on the capacity of the gel resin.

Table 27

REMOVAL OF ANTIMONY AND ARSENIC FROM EFFLUENT: TESTS 30 TO 33

Test	Resin Type form	Resin Vol. mL	Effluent Bed Volumes	Antimony Solution, mg/L Feed	Antimony Solution, mg/L DX	Antimony Loading mg/mL resin
30	MP-500 OH	5	20	25.2	8.1	0.34
31	MP-500 OH ground	5	20	25.2	6.7	0.37
32	IRA-400 OH	5	20	25.2	3.8	0.43
33	IRA-400 OH ground	5	20	25.2	3.4	0.44

In summary, thirty-three tests were carried out in an attempt to find conditions under which an ion exchange resin might remove antimony and arsenic efficiently from mill effluent solutions. Both macroporous and gel anionic exchange resins in a variety of forms were tested, as well as one cationic exchange resin. Attempts were made to alter the speciation of the complexes by altering the pH and redox potential of the mill effluent prior to contact with the resin.

In all cases, the loading efficiencies were poor. For the feed effluent tested (25 to 40 mg/L Sb), antimony loaded to about 0.14 mg/mL resin when contacted batchwise with 5 bed volumes of effluent, and to 1 mg/mL resin when contacted batchwise with 50 bed volumes of effluent. Under these conditons, breakthrough would occur within 3 bed volumes.

The NaCN levels during washing with 1% sulphuric acid never exceeded 100 ppm NaCN for either column. After 5.3 bed volumes of dilute acid had passed through the first column, the NaCN level in the eluate was 50 ppm. Washing of the first column was terminated at this point. The NaCN level in the eluate from the second column was reduced to 2 ppm after 24 bed volumes of 1% sulphuric acid had passed through the column. Little change was observed after this and the acid washing process was stopped. Both columns were rinsed well with water before the loading of the alkaline cyanide solution was initiated.

A lime solution containing 100 ppm NaCN was then passed through each column. The eluate from each column was collected in 500 mL batches and assayed for cyanide until the first trace of cyanide was detected.

The first column, which had been washed to only 50 ppm NaCN, had detectable levels of cyanide (0.25 mg/L) present in the first 500 mL sample (6.7 bed volumes). The second column, which had been washed to less than 2 ppm NaCN also had detectable levels of cyanide (0.18 mg/L) present in the first 500 mL samples (4 bed volumes). Careful washing of the resin after preconditioning with cuprocyanide may reduce, but will not eliminate, the "royal barren" behaviour observed by Gilmore. In the remainder of the work reported in this paper, 1% sulphuric acid washing of the treated resin was carried out until the concentration of cyanide leaking from the column remained constant, typically less than 5 ppm CN. The resin was then washed with copious amounts of water.

A.III.3.0 COLUMN II - TESTWORK

A.III.3.1 Background

The first column of the two column system was designed to remove the metal cyanide complexes from cyanide waste solution. The second column, consisting of a strong base resin in the sulphate form preconditioned with cuprocyanide, was tested for the removal of free cyanide from the resulting effluent. In the 1976 report by A. J. Gilmore (12), a "royal barren" typically occurred during the inital bed volumes of effluent from the secondary column. This "royal barren" contained cyanide, and in most cases copper. It was concluded that unadsorbed free cyanide was dissolving the copper cyanide on the secondary column. Although the "royal barren" could be recycled, the report tested and recommended the operation of two sulphate columns in series as being more efficient at achieving effluent containing less than 0.1 ppm CN(t), than operation of the cuprocyanide form of the resin for the second column.

Witteck undertook to reinvestigate the efficiency (loading capacity, barren levels) of the cuprocyanide resin in producing effluent containing less than 0.1 ppm CN(t), and to compare it to other forms of a strong base resin. The investigation centred on three aspects of the operation: the preconditioning stage, the bleeding of cyanide during loading, and the removal of copper during loading and stripping. The results of this testwork are reported in Appendix III Sections 3.2 and 3.3. The results of the testwork on other forms of anionic exchange resins are reported in Appendix III Section 3.4.

A.III.3.2 Preconditioning Step

In the 1976 CANMET report, Goldblatt's method of preconditioning the column was used. Goldblatt (2) states that once the resin was loaded with copper cyanide, it was washed with water and eluted with 1% sulphuric acid until the cyanide concentration in the eluate dropped to less than 1000 mg/L NaCN. The column, after water washing, was ready for adsorption of free cyanide. There was no indication of the concentration of cyanide in the column eluate during or following the water wash. Witteck suspected that elution with dilute acid to less than 1000 mg/L NaCN in the eluate was insufficent, as a free cyanide concentration below 0.1 mg/L was desired in the column effluent during the loading cycle. Witteck decided to investigate if prolonged elution with dilute acid followed by water would produce an eluate with significantly lower cyanide concentrations, and if so, if this would reduce or eliminate the leakage of copper and cyanide from the column during the initial bed volumes of the loading cycle.

Amberlite IRA-400 in the sulphate form was converted to the cuprocyanide form by conditioning the chloride form with a cuprocyanide solution, as described by Goldblatt (2). After the copper cyanide solution had percolated through the column overnight, the resin was washed well with water. Initially, the wash water contained approximately 100 mg/L NaCN, but continued washing reduced the NaCN in the column wash eluate to less than 10 mg/L NaCN. At this point the resin was removed from the column, well mixed, and divided into two columns. The first column was to be washed with 1% sulphuric acid until the NaCN level in the eluate dropped to less than 1 g/L, as recommended by Goldblatt. The second column was to be washed with 1% sulphuric acid, until the leakage of NaCN reached a constant minimal value.

0700A

WD1

A.III.3.3 Cyclic Testwork - Cyanide Levels in Barrens, Breakthrough and Equilibrium Capacity and Loss of Copper from Preconditioned Resin

In the 1976 CANMET report (12), Gilmore carried out one adsorption/elution cycle for each of six mill effluents. During the initial loading cycle, royal barren behaviour was observed. Since careful cleaning of the preconditioned resin did not eliminate this occurrence, cyclic adsorption/elution testwork was carried out to determine if the leakage of cyanide and copper from the cuprocyanide resin might decrease with subsequent cycles.

Six adsorption/elution cycles were carried out during the test program. In addition to following the cyanide and copper levels in the column effluent, the leakage of copper from the column during stripping was monitored in order to quantify the amount of copper removed during each cycle. This would be expected to affect both the loading capacity and the frequency of reconditoning the resin.

The cyprocyanide form of Amberlite IRA-400 was prepared as described by Goldblatt (2), and washed with 1% sulphuric acid and water as described above Appendix III Section 3.2. During the preconditioning and washing stage, copper concentrations in all solutions were monitored. The final loading of copper on the preconditioned resin was 20 mg Cu/mL resin or 39 mg Cu/g resin.

The cuprocyanide form of the resin (50 mL) was placed in a column (2 cm diameter). A solution of sodium cyanide (510 mg/L CN), adjusted to pH 11 with sodium hydroxide, was passed downflow through the column at the feed rate of 12.5 mL/min.

Loading was continued until the concentration of cyanide in the column effluent approached that of the feed solution. After each load cycle the column was washed with approximately two bed volumes of water.

To strip, a solution of dilute sulphuric acid (pH 1.5; 1000 mL) was recirculated downflow through the ion exchange column. The vessel containing the acidic regenerant solution was sealed. Air was sparged continuously through the regenerant solution and was scrubbed of HCN by passage through an alkaline trap. The trap was maintained at a pH of at least 12 by the periodic addition of sodium hydroxide. Elution was continued until the amount of cyanide in the alkaline trap reached a maximum constant value.

During each loading cycle, the column effluent was sampled periodically. In order to determine if breakthrough capacity increased with subsequent cycles (i.e. if royal barren behaviour was a first cycle phenomena), the individual samples taken during the first, fifth and sixth cycles were assayed for total cyanide and copper, to produce loading isotherms. For each adsorption cycle, the individual samples taken during loading were combined to form one composite sample of the column effluent. Comparison of the composition of the composite effluent sample to that of the feed solution determined the total amount of cyanide loaded and the total amount of copper removed during each loading cycle.

The amount of cyanide and copper removed from the resin during each elution cycle was determined by assaying the alkaline trap for cyanide and the regenerant solution for copper and cyanide. The amount of cyanide remaining in the regenerant solution at the end of an elution cycle was less than 5% of the total cyanide. For each loading/stripping cycle, the percent recovery of cyanide was determined.

0700A

WD1

In order to observe any net loss in equilibrium capacity after six cycles due to loss of copper from the resin, care was taken during the first and final cycles to ensure that full equilibrium capacity was achieved. A summary of the amount of cyanide loaded during each cycle, the percent cyanide recovered and the amount of copper removed from the resin during each stage is provided in Table 28.

Cyanide Recovery

The percent cyanide recovered for each cycle varied from 90 to 99.9%. The overall recovery of cyanide after six loading and elution cycles was greater than 95%.

Equilibrium Capacity - Loss of Copper from Resin

The amount of cyanide loaded during each cycle varied. For the first and final cycles, where full equilibrium loading capacity was achieved, the final equilibrium capacity (29.2 mg CN/mL resin) was 92.6% of that observed during the first cycle (31.5 mg CN/mL resin). The amount of copper remaining on the resin prior to the sixth cycle was 81% of the copper present after the preconditioning step. Loss of cuprocyanide from the resin will return those sites on the resin to the sulphate form after each elution cycle. In Appendix III Section 3.4, a comparison is provided between the equilibrium capacities of the cuprocyanide and sulphate forms of the resin for uncomplexed cyanide. The sulphate form was found to have 70% of the equilibrium capacity of the cuprocyanide form. On this basis, one can calculate that an 80:20% mixture of the cuprocyanide and sulphate forms of the resin should show approximately 94% of the equilibrium capacity of the cuprocyanide form alone. This is in good agreement with the observed 92.6%.

0700A

WD1

Table 28

CYCLIC TESTWORK: COLUMN II

Stage	Time min.	Cyanide Loaded mg	Cyanide Recovered mg	Cyanide Recovered %	Copper Removed mg	Copper Remaining mg
Precondition	-	-	-	-	-	1017
Load 1	360	1575	-	-	8	1009
Strip 1	430	-	1540	97.8	53	956
Load 2	260	1398	-	-	2	954
Strip 2	407	-	1396	99.9	22	932
Load 3	270	1418	-	-	7	925
Strip 3	420	-	1411	99.5	70	855
Load 4	270	1353	-	-	19	836
Strip 4	380	-	1266	90.5	2	834
Load 5	265	1259	-	-	5	829
Strip 5	540	-	1189	94.4	2	827
Load 6	317	1458	-	-	5	822
Strip 6	460	-	1331	91.3	1	821
Overall		8463	8093	95.6	196	821

The amount of copper removed during each loading cycle showed no obvious trend, varying from 8 to 20 mg of copper per cycle. The amount of copper removed during the elution cycles appeared to decrease with time. If the cuprocyanide form of the resin were used in a full scale operation, the frequency of reconditioning the resin would depend on the percent optimal loading capacity specified by the design criteria. If 95% of optimal capacity was specified, the resin may have to be reconditioned approximately every 6 cycles. Further research would have to be undertaken to determine the frequency of the reconditioning step if lower optimal loading capacities could be tolerated.

Loading Isotherms : Royal Barren Behaviour and Breakthrough Capacity

The loading isotherms for the first, fifth and sixth cycles are provided in Figures 18 to 20. The data is listed in Tables 29 to 31. For all three cycles, the total cyanide in the column effluent was greater than or equal to 0.1 ppm CN(t) in the first sample taken, and increased up to 0.3 or 0.4 ppm CN(t) by 5 or 7.5 bed volumes. After this initial rise, a sharp decrease was observed in CN(t) concentration, down to 0.10, 0.18 and 0.05 ppm CN(t) for cycles 1, 5 and 6 respectively. After this drop, the cyanide level increased slowly up to approximately 1 ppm CN(t) by 30 to 40 bed volumes, followed by a rapid increase in cyanide concentrations once the 1 ppm cyanide level was passed.

The behaviour observed during the first cycle was very similar to the royal barren described by Gilmore (12). In the present study, the column effluent assay never dropped below 0.1 ppm CN(t). While it was hoped that subsequent samples might show a

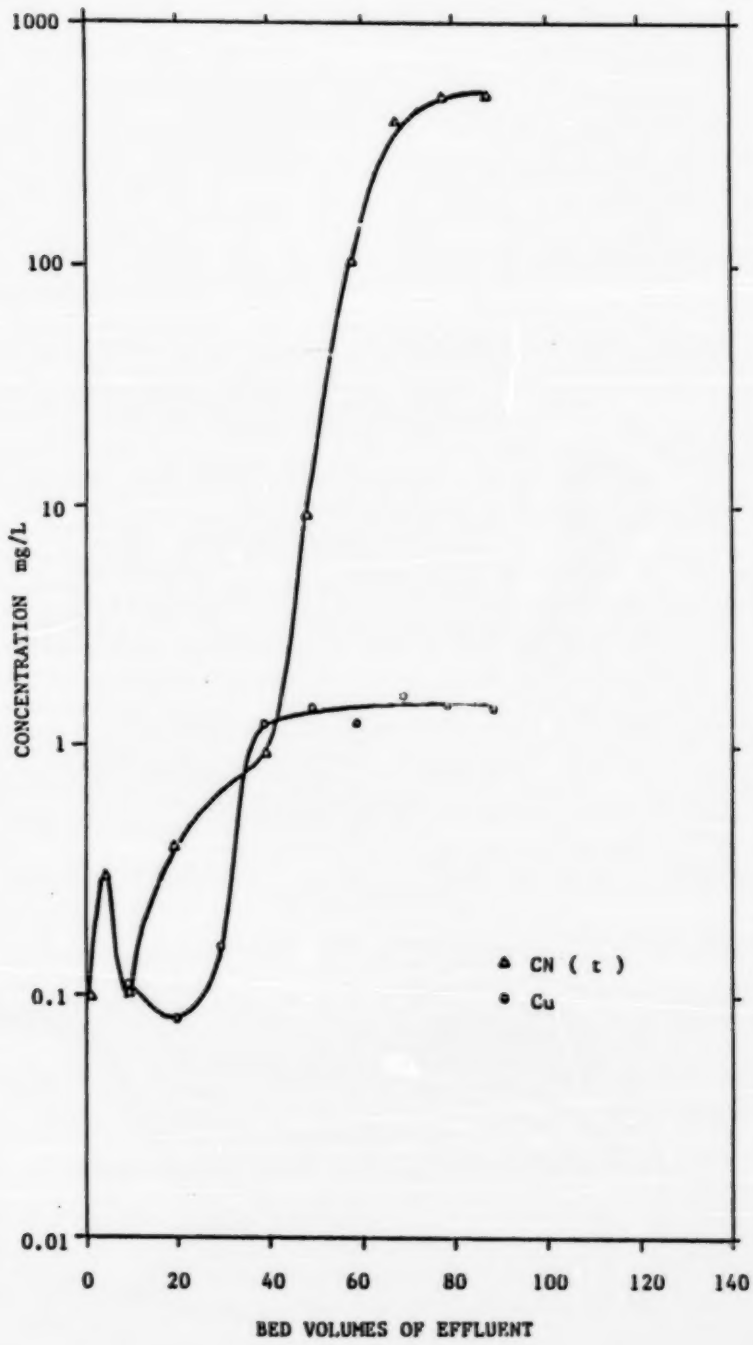


FIGURE 18: LOADING ISOTHERM FOR CYCLE 1
OF COLUMN 2 TESTWORK

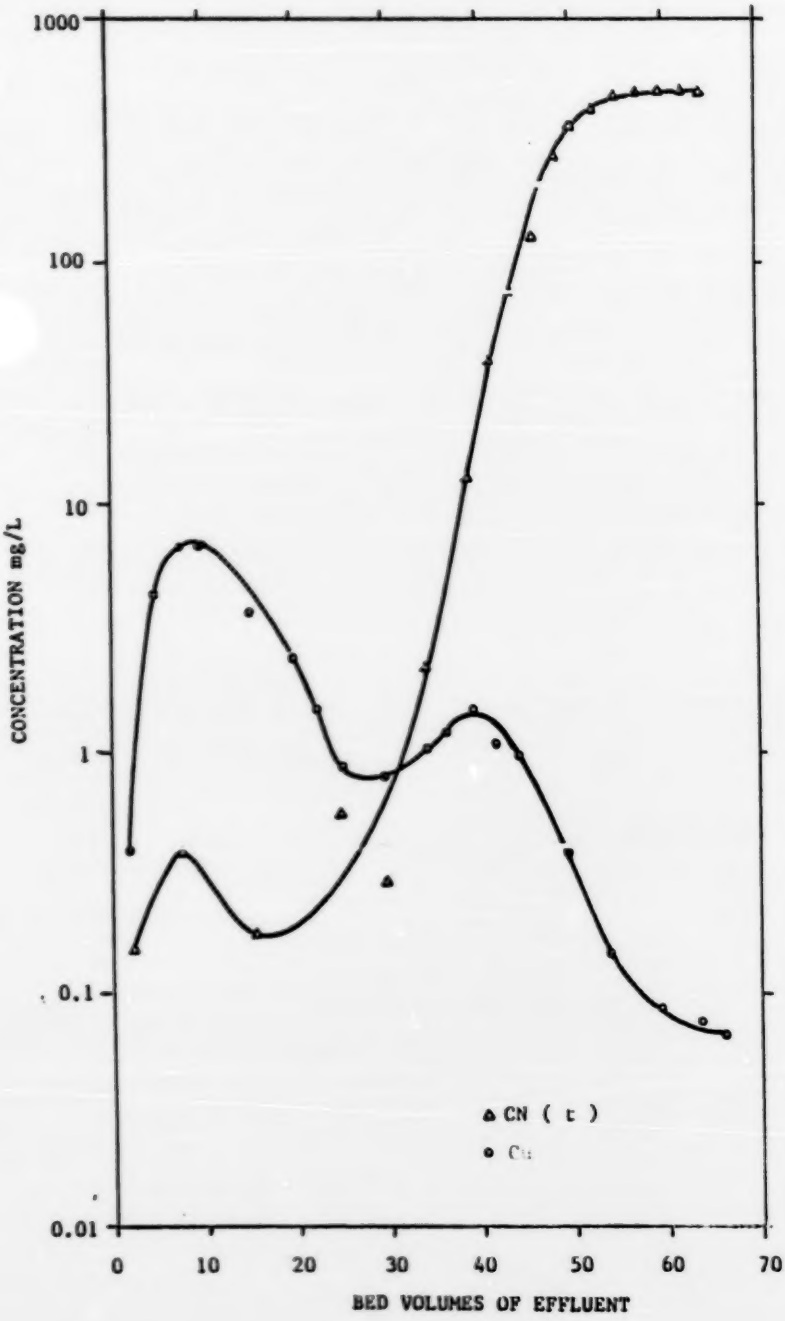


FIGURE 19: LOADING ISOTHERM FOR CYCLE 5 OF COLUMN 2 TESTWORK

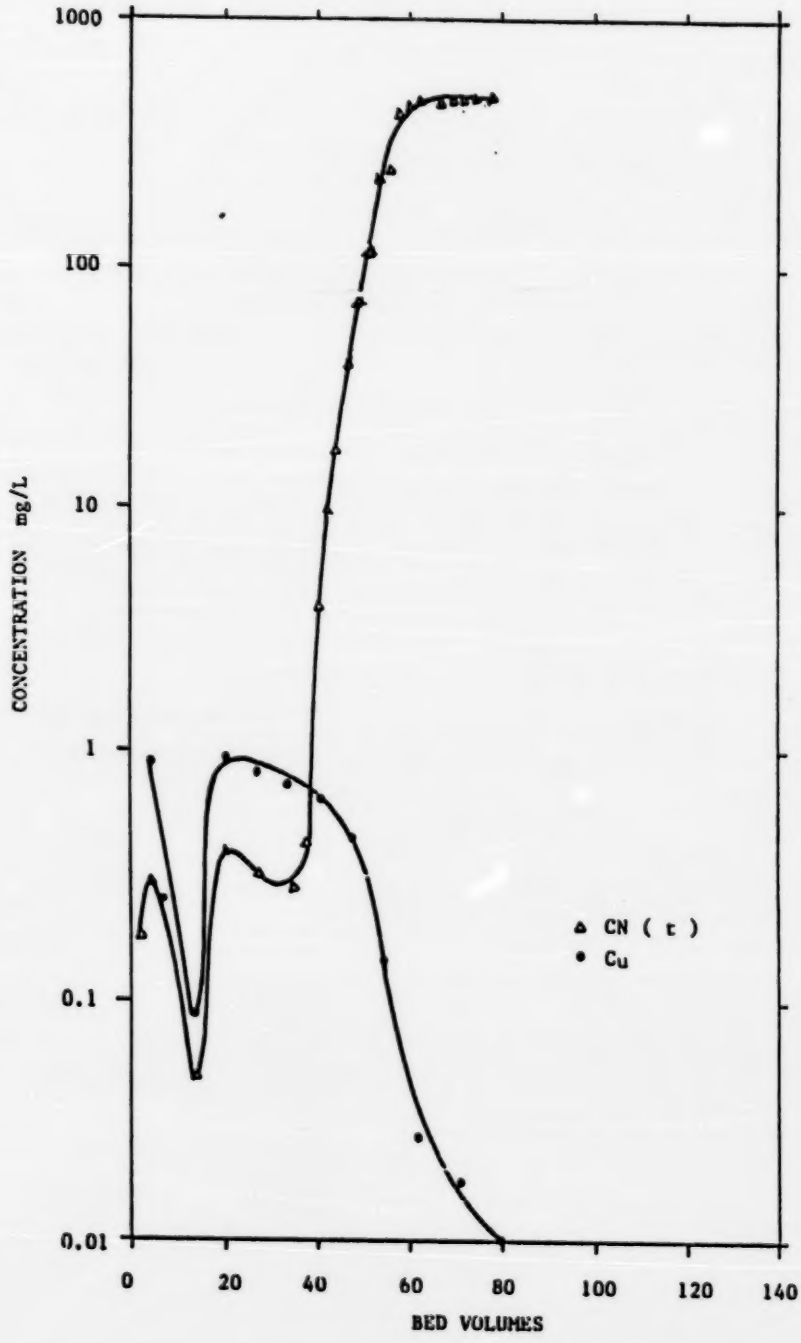


FIGURE 20: LOADING ISOTHERM FOR CYCLE 6 OF COLUMN 2 TESTWORK

Table 29

CYCLE I : LOADING OF COLUMN II

Flowrate	: 12.5 mL/min
Bed Volume	: 50 mL
Column Diameter	: 2 cm I.D.
Feed Solution	: pH 11; 500 ppm CN_T

Run Time Min	Volume of Eluate mL	BV	pH of Eluate	Analysis of Eluate CN_T	Cu
10	125	2.5	7.6	0.10	-
20	250	5	8.0	0.30	-
40	500	10	9.3	0.10	0.10
80	1000	20	10.8	0.40	0.08
120	1500	30	11.0	-	0.16
160	2000	40	11.1	0.95	1.23
200	2500	50	11.1	9.00	1.45
240	3000	60	11.1	11.70	1.25
280	3500	70	11.1	385	1.62
320	4000	80	11.0	489	1.60
360	4500	90	11.0	510	1.55

Table 30

CYCLE 5 : LOADING OF COLUMN II

Flowrate : 12.5 mL/min
Bed Volume : 50 mL
Column Diameter : 2 cm
Feed Solution : pH 11; 520 ppm CN_T

Run Time Min	Volume of Eluate		Analysis of Eluate	
	mL	BV	CN_T	Cu
10	125	2.5	0.15	0.4
22	275	5.5	-	4.3
33	412	8.2	0.40	6.6
43	438	10.8	-	6.8
64	800	16.0	0.18	3.7
83	1038	20.8	-	2.43
93	1162	23.2	-	1.53
103	1288	25.8	0.57	0.89
122	1525	30.5	0.30	0.84
140	1750	35.0	2.23	1.06
150	1875	37.5	-	1.23
160	2000	40.0	13	1.51
170	2125	42.5	40	1.07
180	2250	45.0	78	1.00
190	2375	47.5	130	-
200	2500	50.0	270	0.4
207	2588	51.8	370	-
217	2712	54.2	430	0.15
227	2838	56.8	480	-
236	2950	59.0	500	0.09
246	3075	61.5	505	-
255	3188	63.8	510	0.08
265	3312	66.2	62	0.07

Table 31

CYCLE 6 : LOADING OF COLUMN II

Flowrate : 12.5 mL/min
Bed Volume : 50 mL
Column Diameter : 2 cm
Feed Solution : pH 11; 500 ppm CN_T

Run Time Min	Volume of Eluate mL	Volume of Eluate BV	pH of Eluate	Analysis of Eluate CN_T	Analysis of Eluate Cu
10	125	2.5	4.4	0.18	0.90
20	250	5.0	4.8	0.30	-
29	362	7.2	4.9	-	0.26
57	712	14.2	6.8	0.05	0.09
84	1050	21.0	10.6	0.40	0.95
111	1388	27.8	10.7	0.33	0.84
138	1725	34.5	10.8	0.30	0.76
157	1962	39.2	10.9	0.45	na
166	2075	41.5	10.9	4.00	0.66
175	2188	43.8	10.9	10	-
184	2300	46.0	10.9	18	-
194	2425	48.5	10.9	40	0.46
203	2538	50.8	10.9	78	-
213	2662	53.2	10.9	123	-
222	2775	55.5	10.9	233	0.15
231	2888	57.8	10.8	355	-
240	3000	60.0	10.8	422	-
249	3112	62.2	10.8	455	0.03
258	3225	64.5	10.8	470	-
276	3450	69.0	10.7	470	-
285	3562	71.2	10.7	480	0.02
294	3675	73.5	10.7	490	-
303	3788	75.8	10.6	490	-
317	3962	79.2	10.6	500	0.01

0700A

decline or disappearance of the royal barren behaviour, such was not the case. Cycles 5 and 6 showed similar behaviour, with the CN(t) concentration dropping only briefly below 0.1 ppm CN(t) during cycle 6.

While the cuprocyanide form of the resin would not be adequate where government guidelines specify discharge concentrations of less than 0.1 ppm CN(t), it would provide adequate equilibrium and breakthrough capacity for cyanide where the government specification was less than 1 ppm [illegible]. For cycles 1, 5 and 6, respectively, the breakthrough capacities [less than 1 ppm CN(t)] for cyanide were 20.4, 15.9 and 20.4 mg CN(t) per mL resin.

Copper Levels in Column Effluent

The copper levels in the column effluent are also given in Figures 18 to 20. During the initial load cycle, the copper levels increased from approximately 0.1 ppm Cu, and maintained a fairly constant level between 1 and 2 ppm Cu after cyanide breakthrough [1 ppm CN(t)]. In cycles 5 and 6, however, the copper levels tend to roughly mimic the cyanide curve up until cyanide breakthrough, reaching levels in excess of 1 ppm Cu. After cyanide breakthrough, the copper levels in the column effluent drop off rapidly to less than 0.1 ppm Cu. The proposed guideline for copper as quoted by Gilmore (12) was 0.3 ppm Cu. Therefore, not only the leakage of cyanide, but the leakage of copper during loading by itself would prohibit discharge of the column effluent prior to cyanide breakthrough.

A.III.3.4 Other Forms of Amberlite IRA-400

In addition to reinvestigating the use of the cuprocyanide form of the resin, two other forms of Amberlite IRA-400 were tested: the sulphate and hydroxide forms. The former was recommended by Gilmore(12) as being more efficient than the cuprocyanide form at achieving column effluent containing less than 0.1 ppm CN(t). The latter was chosen since hydroxide anion typically has a lower affinity for strong base anionic exchange resins than most simple anions. On this basis, it might be expected to exchange more effectively with free cyanide.

For the comparison, three columns were set up, each containing Amberlite IRA-400 in the appropriate form. The cuprocyanide form of the resin was prepared as described by Goldblatt (2), and washed with water, eluted with 1% sulphuric acid, followed by further water washing as described above (see Section A.III.3.2). The final loading of copper on the preconditioned resin was 32 mg Cu/mL resin. The sulphate and hydroxide forms of the resin were prepared by treating the chloride form batchwise with approximatly 1M H_2SO_4 and 2M NaOH, respectively, until no chloride was observed in the supernatant. The resin was washed well with water.

The resin (50 mL) was placed in a 2 cm diameter column. A solution of NaCN (510 ppm CN; pH 11 with caustic) was fed through each column at a feed rate of 12.5 mL/min. Samples were taken periodically from the column effluent and assayed for total cyanide. For the cuprocyanide form of the resin, copper assays were also performed.

The data obtained is provided in Figures 21 and 22 and Table 32. Figure 21 shows the general shape of the three loading isotherms after breakthrough. The hydroxide and cuprocyanide forms of the resin show sharper loading behaviour than does the sulphate resin. For the latter, the cyanide level in the column effluent remained below 1 ppm CN(t) level for the first 15 bed volumes. After this, the loading curve has a gradual slope; the resin remaining not fully loaded after 140 bed volumes. At the same feed rate, the hydroxide and cuprocyanide forms of the resin displayed better loading isotherms, remaining below 1 ppm CN(t) for the first 30 and 40 bed volumes, respectively, and thereafter rising quickly to achieve equilibrium loading capacity within 70 and 90 bed volumes, respectively.

The cyanide levels prior to breakthrough are shown more clearly in the semilogarithmic plot provided in Figure 22. The breakthrough and equilibrium capacities for the three resins are summarized in Table 33.

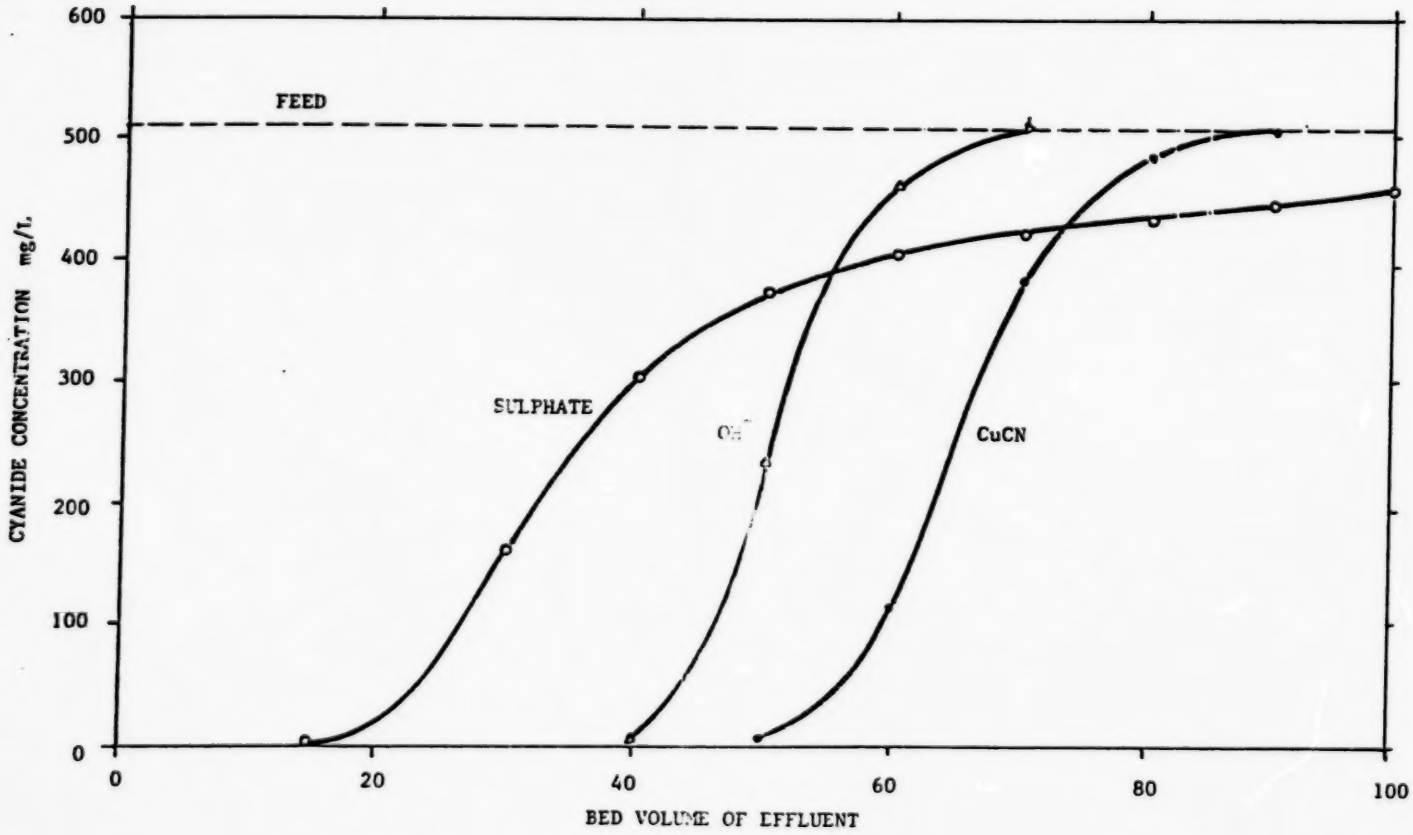


FIGURE 21 : LOADING ISOTHERMS FOR SULPHATE, HYDROXIDE AND CUPROCYANIDE FORMS OF IRA-400

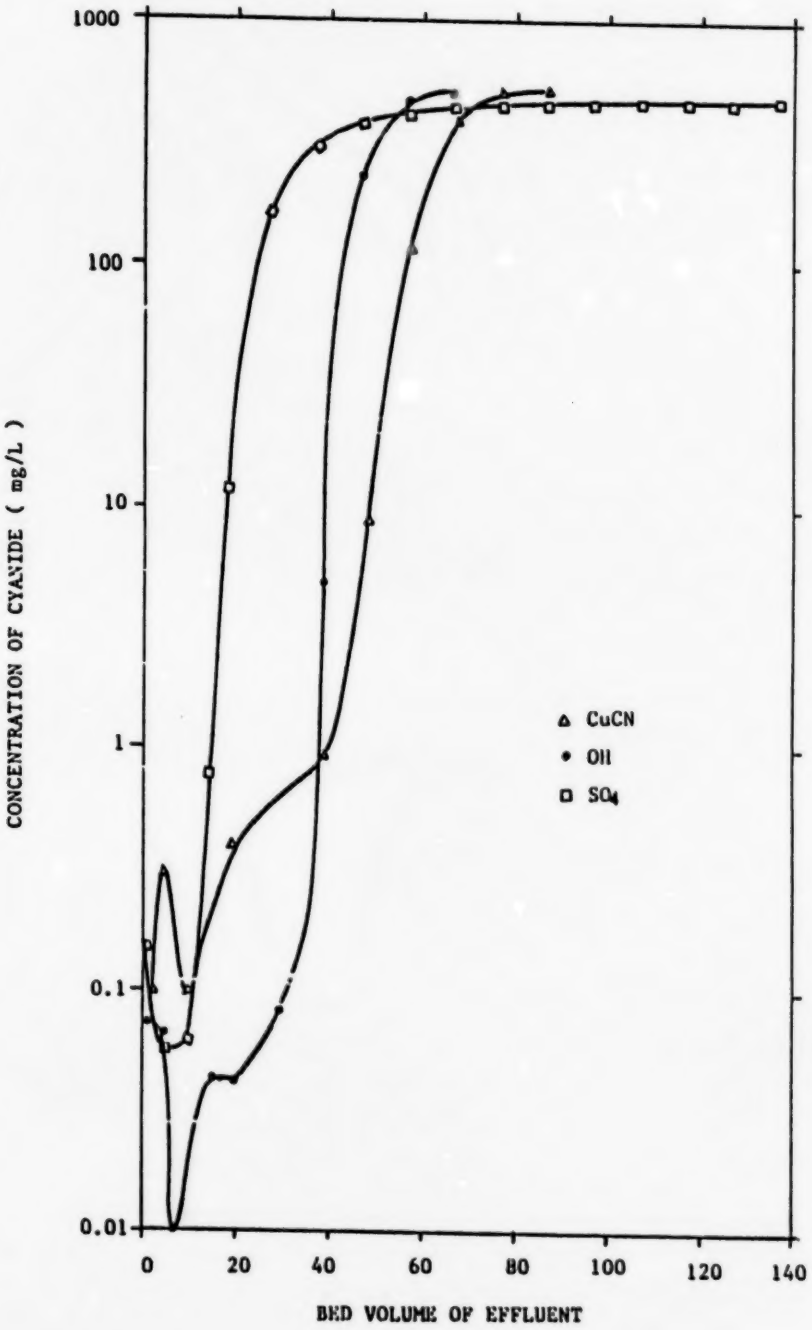


FIGURE 22: LOADING ISOTHERMS FOR SULPHATE, HYDROXIDE & CUPROCYANIDE FORMS OF IRA-400 (SEMI-LOGARITHMIC)

Table 32

COMPARISON OF BREAKTHROUGH AND EQUILIBRIUM LOADING CAPACITIES FOR "CuCN", SULPHATE AND HYDROXIDE FORMS OF AMBERLITE IRA-400

Run Time	Effluent Volume		Column Effluent Analysis, ppm Cu, CN(t)						
			"CuCN" Form			Sulphate		Hydroxide	
min	mL	BV	pH	CN(t)	Cu	pH	CN(t)	pH	CN(t)
4	50	1	7.1	-	-	7.4	0.15	11.0	0.075
8	100	2	7.5			7.7	-	11.9	-
12	150	3	7.7	0.10	1.79	7.9	-	12.0	-
16	200	4	7.9	-	-	8.0	-	12.0	-
20	250	5	8.0	0.30	1.07	8.6	0.056	12.0	0.069
28	350	7	8.4	-	-	10.9	-	12.0	<0.02
40	500	10	9.3	0.10	0.38	10.9	0.063	12.0	-
60	750	15	10.4	-	-	10.9	0.79	12.0	0.044
80	1000	20	10.8	0.40	2.80	10.9	12	12.0	0.044
120	1500	30	11.0	-	2.47	10.9	161	12.0	0.088
160	2000	40	11.1	0.95	2.71	10.9	304	12.0	5
200	2500	50	11.1	9	-	10.9	374	11.6	237
240	3000	60	11.1	117	2.17	10.9	405	11.0	463
280	3500	70	11.1	385	-	10.9	421	11.0	510
320	4000	80	11.0	489	-	10.9	437	-	-
360	4500	90	11.0	510	2.91	11.0	447	-	-
400	5000	100	-	-	-	11.0	458	-	-
440	5500	110	-	-	-	10.9	463	-	-
480	6000	120	-	-	-	10.9	468	-	-
520	6500	130	-	-	-	10.9	468	-	-
560	7000	140	-	-	-	10.9	478	-	-

0700A

WD1

Table 33

COMPARISON OF BREAKTHROUGH AND EQUILIBRIUM CAPACITY

Capacity Level	Capacity mg CN(t)/mL Resin		
	CuCN	SO_4	OH
Breakthrough:			
(a) 0.1 ppm CN(t)	0	5.1	15.3
(b) 1.0 ppm CN(t)	20.4	7.6	15.3
Equilibrium	31.9	n.d.*	25.1

* not determined

The sulphate form of the resin is the poorest at removing cyanide from solution. Although it can achieve less than 0.1 ppm CN(t) for the first 10 bed volumes, the capacity at breakthrough is only 5 mg CN/mL resin.

The cuprocyanide form has the highest capacity at breakthrough, 20 mg CN/mL resin, however, for this resin breakthrough occurs at 1 ppm CN(t), the effluent never achieves less than 0.1 ppm CN(t). Equilibrium capacity for this form of the resin was 32 mg CN/mL resin.

The hydroxide resin was superior on all accounts. It removes cyanide to below 0.1 ppm CN(t), loading to a capacity of 15.3 mg CN/mL resin at breakthrough. Breakthrough occurred sharply after 30 bed volumes. Equilibrium loading capacity was 25 mg CN/mL resin. This resin is recommended for further testwork.

A.III.4.0 COLUMN I AND COLUMN II OPERATED IN SERIES

In the last part of the testwork, column I and II were coupled and operated in series. Column I contained 50 mL of Amberlite IRA-400 in the sulphate form. Column II contained 50 mL of IRA-400 in the sulphate form, preconditioned with cuprocyanide, as described above. All species present in the feed solution were followed during this testwork. The feed effluent was mill barren from Operation B and contained levels of antimony, arsenic and cobalt.

Mill effluent was fed to column I at a feed rate of 12.5 mL/min. The column I effluent was fed directly to column II. Samples of the column I effluent were taken after every 10 bed volumes and assayed for CN(t), SCN, Cu, Fe, Ni, Zn, As, Sb, Co, Mo and Pb. Samples of the column II effluent were sampled periodically for those elements which were not removed entirely from the effluent after passage through column I, i.e. CN(t), SCN, As and Sb. Copper assays were included for column II in order to follow the loss of the copper from the preconditioned resin.

Prior to stripping, each column was washed with water. Stripping of column I was carried out using the Witteck/Lac process. Stripping of column II was carried out using pH 2 sulphuric acid. For both columns, cyanide was trapped using 0.5 N sodium hydroxide as described above. Stripping cycles were carried out for at least 10 hours.

Two loading/stripping cycles were conducted. The head assays and loading data for column I for cycle I and cycle II are provided in Tables 34 and 35. The loading data for column II for the two cycles are provided in Tables 36 and 37. At completion of the last stripping cycle, a representative sample of the resin from each column was assayed. These results are provided in Table 38.

The deportation of each element is discussed below.

Copper, Nickel, Zinc

As shown in Table 34 and 35, copper, nickel and zinc cyanides are efficiently recovered on column I. These elements would not report to column II if the adsorption cycle is halted when metal breakthrough occurs. For the second cycle, these three metals were present in excessive amounts in the first ten bed volumes of column I effluent. This was due to insufficient washing of the column I resin bed after elution, as indicated by the pH of the column effluent, (pH 3). Barren levels of less than 0.1 mg/L can be obtained easily for these metals using ion exchange.

After the second elution cycle, resin analyses indicated that 158 mg Cu, 2.6 mg Ni and 2.9 mg Zn remained on the resin. Compared to the total amounts loaded during cycles 1 plus 2, the percent metals remaining on the resin was: 31% Cu, 0.6% Ni and 0.6% Zn. The low copper recovery during stripping is in disagreement with the results reported in Section 5.2, for Column I testwork. The only variable with respect to the elution and cyclic testwork reported in Section 5.2, was the resin. Amberlite IRA-400, rather than MP-500 was used during this phase of the testwork. It may be that cuprocyanide is not removed as efficiently from the Amberlite IRA-400 resin using the WDI/LAC reagent as it is from the Lewatit MP-500 resin.

Table 34

CYCLIC TESTWORK: COLUMN I LOADING DATA FOR CYCLE I

	Analyses, mg/L										
pH	CN(t)	SCN	Cu	Fe	Ni	Zn	As	Sb	Co	Mo	Pb
Feed											
10.5	617	240	64	14.61	56.0	59.0	8.72	1.34	2.04	0.23	0.14
Column Effluent											
BV											
10	10.1	<0.02	<1	<0.01	<0.01	<0.01	<0.01	5.09	1.24	0.02	<0.01	0.02
20	10.2	46	-	<0.01	<0.01	0.035	<0.01	5.84	1.03	0.03	<0.01	0.02
30	10.4	333	-	<0.01	<0.01	0.046	<0.01	8.12	1.15	0.03	<0.01	<0.01
40	10.5	399	-	<0.01	<0.01	0.065	<0.01	9.97	0.93	0.03	<0.01	0.04
50	10.5	413	-	<0.01	<0.01	0.087	<0.01	10.0	0.79	0.04	<0.01	0.04
60	10.5	416	-	<0.01	<0.01	0.068	<0.01	10.1	0.72	0.04	<0.01	0.04
62	10.5	416	<1	<0.01	<0.01	0.025	<0.01	10.5	1.02	0.04	<0.01	-
Resin Loading, mg		1222	804	214	49	187	198	2.30	1.12	6.7	0.77	0.35

Table 35

CYCLIC TESTWORK: COLUMN I LOADING DATA FOR CYCLE II

	Analyses, mg/L										
pH	CN(t)	SCN	Cu	Fe	Ni	Zn	As	Sb	Co	Mo	Pb
Feed											
10.6	506	275	66	16.7	49.0	60.0	9.39	1.36	2.20	0.18	0.03
Column Effluent											
BV											
10	2.9	4.3	<1	0.65	<0.01	0.15	0.72	7.12	1.27	0.04	<0.004	0.03
20	6.2	5.0	-	-	-	-	-	-	-	-	-	-
30	9.0	52	<1	<0.01	0.02	0.05	0.04	10.0	1.25	0.04	0.12	0.04
40	10.5	395	-	-	-	-	-	-	-	-	-	-
50	10.6	395	-	-	-	-	-	-	-	-	-	-
60	10.6	400	<1	<0.01	0.02	<0.01	0.02	11.0	0.96	0.04	0.24	0.02
70	10.6	395	20	-	-	-	-	-	-	-	-	-
80	10.5	343	500	-	-	-	-	-	-	-	-	-
90	10.5	312	700	0.12	0.13	<0.01	0.05	9.62	0.83	0.05	0.29	0.03
Resin Loading, mg		1203	803	297	75	220	270	-1.15	1.22	9.8	0.08	0
Total, mg (cycle 1 + 2)		2425	1607	511	124	407	468	1.15	2.34	16.5	0.85	0.35

Table 36

CYCLIC TESTWORK: COLUMN II LOADING DATA FOR CYCLE I

Eluate, BV	pH	Analyses, mg/L CN(t)	SCN	Cu	As	Sb
0-45	10.3	0.13	<1	0.08	0.06	1.35
45	-	-	-	-	0.36	1.78
48	10.5	0.19	<1	0.49	-	-
51	10.5	0.19	<1	0.14	-	-
54	-	-	-	-	3.18	1.49
56	10.5	0.13	<1	0.38	-	-
59	-	-	-	-	5.41	1.55
62	10.5	0.10	<1	0.15	-	-
64	-	-	-	-	9.36	1.60
67	10.5	0.11	<1	0.12	-	-
Resin Loading, mg	-	845	0	0	22	0

Table 37

CYCLIC TESTWORK:COLUMN II LOADING DATA FOR CYCLE II

Eluant		Analyses, mg/L				
BV	pH	CN(T)	SCN	Cu	As	Sb
2.4	2.2	11.6	<1	20	1.68	0.05
9.6	2.4	20.8	<1	4.8	3.65	0.58
21.8	2.5	7.2	<1	2.6	3.90	0.79
32.5	3.4	1.11	<1	1.8	3.29	0.94
43.5	9.4	0.02	<1	0.24	2.85	1.50
53.9	10.0	0.02	<1	0.35	3.64	1.38
64.6	10.1	0.02	<1	0.34	5.15	1.37
77.7	10.3	0.02	<1	0.42	11.2	1.33
90.8	10.5	0.02	<1	0.52	17.7	1.38
Resin Loading, mg		1055	435	0	15	0
Total, mg (Cycle 1 + 2)		1900	435	0	37	0

Table 38

RESIN ANALYSES AFTER TWO LOADING/STRIPPING CYCLES

	Analyses, mg								
	CN(t)	SCN	Cu	Fe	Ni	Zn	As	Sb	Co
Column I	593	1.6	158	74	2.6	2.9	<0.01	<0.01	3.4
Column II	154	<1.3	1293	-	-	-	1.4	<0.01	-

0700A

Iron, Cobalt and Lead

Iron, cobalt and lead are also recovered efficiently by the first column, producing a column effluent containing less than 0.02 mg/L Fe, 0.05 mg/L Co and 0.04 mg/L Pb. However, iron and cobalt were not removed during stripping, but acted as resin poisoning agents under these conditions. Resin analyses indicated that 60% of the Fe and 21% of the cobalt remained in the resin after two cycles. Lead analyses were not performed on the stripped resin due to the very low quantity loaded after two cycles (0.35 mg/50 mL resin).

Molybdenum

Molybdenum was recovered efficiently on the primary column during the first cycle, but broke through during the loading of the second cycle. The total amount of molybdenum loaded after two cycles was 0.85 mg/50 mL resin. Resin analyses did not provide an accurate molydenum assay to determine if molybdenum is acting as a poison. Further testwork on an effluent solution containing a higher concentration of molybdenum would be necessary to follow the deportment of this element.

Arsenic and Antimony

Neither arsenic nor antimony loaded efficiently on the primary column. The loading cycles indicated that 1.6% of the arsenic (1.15 mg) and 22% of the antimony (2.34 mg) loaded onto the first column during the two cycles.

Arsenic partially loads during the first few bed volumes but then is displayed by other metal cyanide complexes which have a higher affinity for the resin. Antimony loaded to low capacity. However, as shown in Table 38, the arsenic and antimony remaining on the column I resin after the loading cycles, is removed during the stripping cycles; there was no antimony nor arsenic on the column I resin after the final stripping cycle.

The antimony reporting to column II did not load to any extent on the cuprocyanide form of the resin. However, as with column I, arsenic does load for the first few bed volumes of column II, and is then displayed from the resin, by either cyanide and/or thiocyanate. After two cycles, 52% of the arsenic had loaded onto the second column. This form of the resin is more efficient at arsenic recovery than the sulphate form of the resin. After stripping, only 2% (1.4 mg) of arsenic remained on the resin.

Thiocyanate

As first noted by Gilmore (12), thiocyanate is absorbed onto the primary column, but breaks through prior to cyanide breakthrough. Thiocyanate remaining on the column I resin after each loading cycle is removed during elution, as indicated by the resin analyses for column I in Table 38. The thiocyanate which reports to column II is removed from the solution by the second column, as indicated in Tables 36 and 37. Thiocyanate is also eluted readily from the secondary column during stripping.

Cyanide

In total, column I loaded 2425 mg CN(t), and column II loaded the remaining 845 mg CN. Elution removed 76% of the cyanide from the column I resin, and 82% of the cyanide from the column II resin, according to resin analyses. This is in fair agreement with the analyses of the alkaline traps, which recovered, in total, 86% and 80% of the cyanide from the two columns, respectively, after two cycles.

Column II barrens assayed less than 0.2 mg/L cyanide. Once again, the achievement of less than 0.1 mg/L cyanide using this method seems doubtful.

APPENDIX IV

Cyanide Recovery and Recycle Questionnaire

WITTECK DEVELOPMENT INC.
2640 South Sheridan Way, Mississauga, Ontario, Canada L5J 2M4
Telephone: (416) 823-7381 Telex: 06-982328

Cyanide Recovery and Recycle Questionnaire

MINE: _____

CONTACT PERSON: _____

ADDRESS: _____ TELEPHONE: _____

DAILY TONNAGE: _____

1. Type of Gold Recovery Process
   - Zinc Precipitation ☐
   - Carbon in Pulp ☐

2. Cyanide Treatment Process (Destructive or Recovery)
   - Alkaline Chlorination ☐
   - Hydrogen Peroxide ☐
   - SO_2/air ☐
   - Other (Please Specify) ☐

3. Effluent Recycle
   - Direct from Mill Barrens ☐
   - From Tailings Area ☐
   - Volume of Recycle per day _____
   - Location of Recycle addition _____
   - No Recycle (please comment reason why) ☐

   _____

4. Approximate Volume and Concentration of Effluent discharge to Tailings area (prior to cyanide treatment)

   Volume of Effluent:

   Analyses of Effluent

   Cyanide, total :

   Cyanide, free :

   SCN :

   Cu :

   Fe :

   Zn :

   Other elements of environmental concern :

5. Approximate Volume and Concentration of Effluent discharge to Environment from Tailings

   Volume of Effluent :

   Analyses of Effluent

   Cyanide, total :

   Cyanide, free :

   SCN :

   Cu :

   Fe :

   Zn :

   Other elements :

6. Cyanide Consumption:

7. Cyanide Addition Location:

   Added to Mill ☐

   Added to Leach Circuit ☐

8. What cost savings could you achieve by recovering and recycling cyanide?

WDI

Comments:

Please return this questionnaire by January 31, 1986 to Witteck Development Inc. in the return envelope provided.

All information will be treated confidentially and used only for the purpose described.

APPENDIX V

References

REFERENCES

1. Burstall, F.H. et al. Ion excnange process for the recovery of gold from cyanide solution. Ind. Eng. Chem., vol. 45, 1953. P.1648.

2. Goldblatt, E. Recovery of cyanide from waste cyanide solutions by ion exchange. Ind. Eng. Chem., vol. 51, 1959. p. 241.

3. Gilmore, A.J. and Cow, W.A. Cyanide recovery from gold-barren waste solutions: A literature review. Mines Branch Information Circular IC 145, Department of Mines and Technical Surveys, Ottawa, Canada, @ 1963.

4. Sloan, W.J. Ion exchange removal of cyanide values. U.S. Pat. 3 656 893, 1972.

5. Shimamura, I. and Iwano, H. Process for treating waste photographic processing solutions. U.S. Pat. 3 869 383, 1975.

6. Fries, W. Selective separation of cyanide from waste streams by adsorption process. U.S. Pat. 3 788 983, 1974.

7. Avery, N.L. and Fries, W. Selective removal of cyanide from industrial waste effluents with ion-exchange resins. I & EC Product Research and Development, vol. 14, 1975. p. 102.

8. Moore, F.L. An improved ion exchange resin method for removal and recovery of zinc cyanide and cyanide from electroplating wastes. J. Environ. Sci. Health, All (7), 1976. p. 459.

WD1

9. Avery, N.L. and Waitz, W.H. Ion exchange treatment process for selective removal of cyanide. Amber-hi-lites, Rohm and Haas, @ 1975.

10. Avery, N.L. Selective removal of iron cyanide anions from fluids containing thiocyanates. U.S. Pat. 4 115 260, 1978.

11. Fries, W. Process for selective removal and recovery of cyanide values by ion exchange. U.S. Pat. 3 984 314, 1976.

12. Gilmore, A.J. The removal of cyanide and metal-cyanide complexes from cyanidation wastes by fixed-bed ion-exchange technology. Mineral Sciences Laboratories Report MRP/MSL (CF) 76-19 (IR), Canada Centre for Mineral and Energy Technology, 1976.

13. Gilmore, A.J. The ion-exchange removal of cyanide from gold-mill wastes for environmental benefit. Mineral Sciences Laboratories Report MRP/MSL (CF) 76-26 (IR), Canada Centre for Mineral and Energy Technology, 1976.

14. Ritcey, G.M. and McNamara, V.M. Treatment of gold mill effluents for removal and recovery or destruction of cyanide - A summary of the joint project with six gold mills. Proceedings of the Tenth Annual Meeting of the Canadian Mineral Processors, Ottawa, January 24 - 26, 1978. p. 152.

15. Trachtenberg, J.J. and Murphy, M.A. Removal of iron cyanide complexes from waste water utilizing an ion exchange process. TMS paper selection LM-79-50, The Metallurgical Society of AIME, @ 1979.

16. Crits, G.J. Cyanide recovery. U.S. Pat. 4 267 159, 1981.

17. Carlson, L.G. Ion exchange treatment for removing toxic metals and cyanide values from waste waters. U.S. Pat. 4 321 145, 1982.

18. Fleming, C.A. Novel process for recovery of gold cyanide from strong base resins. Extraction Metallurgy Symposium, Institute of Mining and Metallurgy, London, September 9-12, 1985.

19. Witte, M.K. Personal Communication.

20. Pourbaix, M. et al. Electrochemical behaviour of arsenic. Potential - pH equilibrium diagrams for the system arsenic - water at 25°C. Technical Report 46, Cebelcor, 1957.

21. Pourbaix, M. et al. Electrochemical behaviour of antimony. Potential - pH equilibrium diagrams for the system antimony - water at 25°C. Technical Report 55, Cebelcor, 1957.